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TITLE

Experimental and Thermo-Economic Analysis of Catalytic Gasification and Fuel Cell Power Systems

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Abstract

This dissertation presents a comprehensive experimental and thermo-economic evaluation of coal gasifiers with *in-situ* carbon capture for generating high-hydrogen and high-methane content syngas for solid oxide fuel cell power plants. The goals of this thesis were the following: to conduct lab-scale experiments on catalytic coal gasification with *in situ* capture of acid gases, such as CO₂ and H₂S; to use the experimental results to model a commercial scale catalytic, *in situ* capture, coal/waste gasifiers; to integrates this gasifier with a solid oxide fuel cell (SOFC) system and to an build economic model to determine the internal rate of return on investment (IRR) of this system; then to compare the IRR of these power plant designs with other fossil fuel based power plant designs with CO₂ capture and sequestration (CCS); and finally, to use the techniques/models developed here create an economic model of a SOFC fueled by an anaerobic digester. In this thesis, we estimate what range of economic parameters, such as SOFC stack capital cost, electricity sale price, and capacity factor, are required so that the systems analyzed can obtain unsubsidized, positive rates of returns on investment. The following are the highlights from each of the chapters.

First, a molten catalytic process has been demonstrated for converting coal into a synthesis gas consisting of roughly 20% methane and 80% hydrogen using alkali hydroxides as both catalysts and *in situ* CO₂ & H₂S capture agents. Baselines studies were also conducted using no catalyst, a weak capture agents (CaSiO₃) and strong *in situ* capture agents for acid gases (NaOH, KOH & CaO). Parametric studies were conducted to understand the effects of temperature, pressure, catalyst composition, steam flow rate and the coal-to-catalyst ratio on the performance of the catalytic gasifier in terms of kinetics and syngas composition. Second, we conducted multi-cycle studies in which CaCO₃ was calcined by heating to 900°C to regenerate the CaO, which was then re-used in repeated CaO-CaCO₃ cycles. We measured increased steam-coal gasification kinetics rates when using both CaO+KOH; these rates persisted even when the material was reused in six cycles of gasification and calcination.

Third, we present an exergy and economic analysis of a power plant system that integrates a CaOlooping gasifier with a pressurized, solid oxide fuel cell (SOFC). We used the gas composition, steamcoal gasification rate and CO_2 capture cycle degradation rate from the previous chapter as input into the model of this CaO-looping gasifier. We conducted an economic analysis of the system as a range of different operating pressures, current densities, fuel utilizations, and air stoichiometric ratios. We calculated an IRR of 6%/yr±4%/yr for the system when the sale price of electricity was \$50/MWh if the CO_2 could be used for enhanced oil recovery (EOR), where the uncertainty accounts only for an estimated uncertainty in the capital costs of +50%/-30%. We conducted a sensitivity analysis to determine the effect of changing some of the assumptions in our cost model, such as the price of the fuel cell stacks, the sale price of CO_2 , the sale price of electricity, the capacity factor, and the fuel price.

Fourth, for comparison, we present exergy and economic analyses of two advanced coal-based power plants configurations in which the CO₂ capture occurs outside of the gasifier. These cases are: an integrated gasification fuel cell cycle with a catalytic gasifier and a pressurized solid oxide fuel cell including CO₂ sequestration (Adv. IGFC-CCS) and an integrated gasification combined cycle with advanced H₂ and O₂ membrane separation including CO₂ sequestration (Adv. IGFC-CCS) using the same economic assumptions, the IRR of the Adv. IGFC-CCS configuration was 4 ± 3 %/yr if the CO₂ can be used for EOR and 1 ± 3 %/yr if the CO₂ can only be sequestered in a saline aquifer. The IRR of the Adv. IGCC-CCS configuration with H₂ and O₂ membrane separation was 8 ± 4 %/yr if the CO₂ can be used for EOR and 3 ± 3 %/yr if the CO₂ must be sequestered in a saline aquifer. Fifth, we compare the IRR of these configurations with the IRR of other fossil fuel power plant configurations. For example, we present results showing which power plant configuration would yield the lowest levelized cost of electricity (LCOE) as a function of the price of CO₂ emissions and a function of the price of natural gas, holding all other variables constant.

Finally, we present an economic analysis of a configuration that uses biogas produced from an anaerobic digester (AD) to fuel a solid oxide fuel cell (SOFC) modeled based off of the pressurized SOFC we developed to the IGFC configurations presented earlier. We performed parametric studies of the AD-SOFC system in order to minimize the normalized capital cost (kW). The four independent variables were the current density, the stack pressure, the fuel utilization, and the total air stoichiometric ratio. Given our economic assumptions, our calculations show that adding a new AD-SOFC system to an existing wastewater treatment (WWT) plant could yield positives values of IRR (9%/yr ±4%/yr at \$80/MWh electricity sale price), and could significantly outcompete other options for using biogas to generate electricity. AD-SOFC systems can convert WWT plants in net generators of electricity rather than net consumers of electricity while generating positives rates of return on investment, based on the assumptions of this analysis.

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Symbol	Units	Definition
'n	mol/s [# / T]	The moles of species "X" per unit time: used for
		amount consumed or amount entering or exiting a
		control volume
Ι	A = C / s [Q / T]	Total current in fuel cell
i	A/cm^2 [Q / L ² ·T]	Current density in the fuel cell
i_o^0	A/cm^2 [Q / L ² ·T]	Exchange current density
Z _X	Dimensionless ratio # ·# · [-]	The ratio of the # of electrons produced or
		consumed in an electrochemical half reaction in
		which species "X" is produced or consumed
F	C/mol [Q/#]	Faraday's Constant = 96,485 coulombs of charge
		per mol of protons
A	m^2 [L ²]	Area, use depends on the context
r	m [L]	Radius, use depends on the context
λ_X	Dimensionless ratio [-]	Stoichiometric ratio (defined separated on both
		the anode and cathode sides) is the ratio of the
		flow rate of oxidant/fuel divided by the rate of
		consumption of the oxidant/fuel. Stoich always
		greater than 1
U	$J \qquad [M \cdot L^2 / T^2]$	Internal Energy is the total energy within a closed
		thermodynamic system, including kinetic,
		rotational, and vibrational motion as well as
		gravitational and chemical potential energy.
û	J/mol $[\mathbf{M} \cdot \mathbf{L}^2 / \# \cdot \mathbf{T}^2]$	Molar internal energy: internal energy per mol
Н	J $[M \cdot L^2 / T^2]$	H = U + pV
		Enthalpy is the internal energy U plus the energy
		required to make room for the system by
		displacing the external environment.
ĥ	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Molar enthalpy: the enthalpy per mol of species

\hat{h}_0	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Molar enthalpy: the enthalpy per mol of species
		at the reference temperature of the environment
G	$J [M \cdot L^2 / T^2]$	G = U - TS + pV
		The Gibbs free energy is the enthalpy minus the
		thermal energy transferred to the external
		environment.
\hat{g}	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Molar gibbs free energy
$g_{formation}$	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Gibbs free energy of formation: is the gibbs free
		energy of a reaction if the reaction were to go
		completely from reactants to products.
Ò	J/s or W $[M \cdot L^2 / T^3]$	Heat Transfer across the control volume. Positive
C C		value corresponds with heat transferred to the
		control volume.
Σċ	J/s or W $[M \cdot L^2 / T^3]$	Sum of all heat transfer across the control
		volume, each of which may occur at different
		temperatures.
Ŵ	J/s or W $[M \cdot L^2 / T^3]$	Power: work generated from the system. Positive
		value corresponds with work done by the system
		on the surroundings. For example, the power is
		defined as positive if electrons leave the system at
		low voltage and return at a higher voltage.
$\sum i \dot{a} $	J/s or W $[M \cdot L^2 / T^3]$	Sum of all power terms: including piston work
		per time, electrical work per time, turbine work
		per time, etc.
S	J/K $[M \cdot L^2 / \Theta \cdot T^2]$	Entropy: $S = k \cdot \ln(\Omega)$
	or	The logarithm of number of equivalent
S/R	dimensionless [-]	microstates in the macrostate with the most
		number of equivalent microstates
ŝ	J/K·mol $[M \cdot L^2 / \# \cdot \Theta \cdot T^2]$	Molar Entropy: entropy per mol of species
Ŝoea	J/K·mol $[M \cdot L^2 / \# \cdot \Theta \cdot T^2]$	Molar entropy of a species at the reference
5,04		temperature of the environment, and at the
		pressure of that species in thermo-chemical
		equilibrium with the environment.
Т	Κ [Θ]	Temperature
	or	
RT	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Inverse slope of the energy distribution function

T ₀	Κ [Θ]	Temperature of the reference environment,
		normally taken to be the Earth's atmosphere
	J/K $[M \cdot L^2 / \Theta \cdot T^3]$	Internal generation of entropy: the production of
	or	entropy within the control volume due to
σ _{irr} /k	s ⁻¹ [1 / T]	irreversible processes.
$\sum \dot{\sigma}_i$	cal/K $[M \cdot L^2 / \Theta \cdot T^3]$	Sum of all internal generation of entropy within
		the control volume due to irreversible processes,
		such as mass, chemical, charge, momentum &
		energy diffusion.
Е	J $[M \cdot L^2 / T^2]$	Exergy of a control volume is the maximum
		useful work that could be generated in bring the
		system into thermal, mechanical and chemical
		equilibrium with the external environment. This
		maximum is achieved via some hypothetical
		reversible process.
ê	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Molar flow exergy: exergy per mol of a species
		or mixture entering or exiting a control volume
Cp	J/K $[M \cdot L^2 / \Theta \cdot T^2]$	Specific heat at constant pressure is defined as the
Ľ	or	change in the enthalpy of a fluid w.r.t. to a
c_p/R	dimensionless [-]	change in temperature at constant pressure.
k	$W/(K \cdot m) [M \cdot L / \Theta \cdot T^3]$	Thermal conductivity
p	J/m^3 [M / L · T ²]	Pressure is defined as minus the change in
		internal energy of system w.r.t. a change in
		volume holding entropy constant.
p_{env}	J/m^3 [M / L · T ²]	The partial pressure of a species in thermo-
		chemical equilibrium with the environment.
D	m^2/s [L ² /T]	Diffusion coefficient or <u>diffusivity</u> : The amount
		of substance diffusing across a unit area due to a
		unit concentration gradient per unit time.
C_X	mol/m^3 [# / L ³]	Concentration of species "X"
u_X		Mobility: the ratio of the drift velocity (due to an
		electric field) divided by the strength of the
		electric field
φ	$V=J/C [M \cdot L^2 / Q \cdot T^2]$	Electric potential: defined as the change in the
		energy of the system with a change in the number
		of charges.

$\Delta \varphi$	$V=J/C [M \cdot L^2 / Q \cdot T^2]$	Open circuit potential: the difference in electric
		potential between the anode and cathode of the
		fuel cell under open circuit conditions.
V	$V=J/C [M \cdot L^2 / Q \cdot T^2]$	This voltage is used for the actual voltage of the
		fuel cell, which is always less than the open
		circuit potential.
<i>K</i> (<i>T</i>)	dimensionless [-]	Equilibrium constant is the product of the
		reactant and product activities raised to the power
		of their stoichiometric coefficient. The
		equilibrium constant is a function of temperature,
		but not a function of pressure.
ν_X	dimensionless [-]	Stoichiometric coefficient is the number of
		molecules of species "X" which participate in the
		reaction as written
a	dimensionless [-]	Activity is the effective concentration of species,
		and the activity is treated as a dimentionless
		quantity by normalizing the effective
		concentration by a reference concentration.
μ	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Molar chemical potential is the change in the
		energy of the system w.r.t. a change in the
		number of species. Depending on whether the
		system is open/closed and whether there is a
		movable wall, the energy can be either of the four
		energies mentioned above, U, H, F, G.
μ	J/mol $[M \cdot L^2 / \# \cdot T^2]$	Molar electrochemical potential is the change in
		the total energy of an ionic species (i.e. chemical
		potential plus electrical potential) w.r.t. a change
		in the number of ionic species.
i_o^0	A/cm ² [Q / L ² ·T]	Exchange current density: the current density of
		the forward and backwards electrochemical
		reaction in equilibrium, which are equal.
α	dimensionless [-]	Symmetry coefficient of the activation barrier of
		the rate limiting step of the electrochemical half-
		reaction. If the peak of the activiation barrier is
		perfectly symmetric, then the value of α should
		be one half ($\frac{1}{2}$).
(<i>αz</i>)	dimensionless [-]	The product of the symmetry coefficient times

		the number of electrons produced/consumed in
		the rate limiting electro-chemical half reaction.
η	$V=J/C [M \cdot L^2 / Q \cdot T^2]$	Activation overpotential: the amount of voltage
		consumed to draw current. The total acativation
		potential is the sum over all irreversible processes
		that cause the actual fuel cell voltage to be less
		than the open circuit potential.
R	$\Omega = \mathbf{J} \cdot \mathbf{s} / \mathbf{C}^2 \qquad [\mathbf{M} \cdot \mathbf{L}^2 / \mathbf{Q}^2 \cdot \mathbf{T}]$	Resistance of the fuel cell
ASR	$\Omega \cdot \mathbf{m}^2 = \mathbf{J} \cdot \mathbf{m}^2 \cdot \mathbf{s} / \mathbf{C}^2$	Area specific resistance is the resistance divided
	$[M\cdot L^4 / Q^2 \cdot T]$	by the active area
$\eta^{compressor}$	dimensionless [-]	Isentropic efficiency of the compressor. Note that
		the symbol is unfortunately the same as for
		overpotential.
$\eta^{turbine}$	dimensionless [-]	Isentropic efficiency of the turbine. Note that the
		symbol is unfortunately the same as for
		overpotential.
IRR	yr ⁻¹ [1 / T]	Internal Rate of Return on Investment

In the Units column, note that: L = Length, M = mass, T = time, # = number (dimensionless), Q = Charge, $\Theta = Temperature$.

Subscripts	
i	Used as an index of summation. Often, the index refers to inlet fluids.
e	Used as an index of summation. Often, the index refers to exiting fluids.
cv	Control volume
0	The variable is taken at a reference state, normally the reference environment
X	Used to denote a generic substance "X"

Chapter 1 Introduction

1.1 Motivation to the Global Energy Problem

"Lastly, I would address one general admonition to all; that they consider what are the true ends of knowledge, and that they seek it not for pleasure of the mind, or for contention, or for superiority to others, or for profit, or fame, or power, or any of these inferior things; but for the benefit and use of Life; and that they perfect and govern it in charity." – Francis Bacon, De Augmentis (1623).

The Earth is a system far-from-equilibrium. It is continuously bathed in a source of exergy in the form of sunlight. Life on earth does not suffer from a lack of potential exergy sources [1] to meet current or future demand for forms of useful work, such as electricity. For example, photosynthesis by plants and microorganisms is only using roughly 90 TW of the 86,000 TW of available surface incident solar exergy [1]. This means that we are nowhere near the limit how much useful work we can extract from sunlight, and likewise, we are nowhere near the limit of how much useful work can be extracted from fossil fuels, crustal geothermal, or nuclear fuels [1].

The global 'energy' problem we face is not due to a lack of exergy, which is plentiful. Generating electricity is not the problem; there are plenty of technologies that can generate electricity. The problem is generating electricity for *more* people, when they want it, at low prices, while limiting environmental damage and while obtaining an unsubsidized, positive real rate of return on investment. The problem can be summarized as follows: how do we develop new technologies in order to reduce the environmental impact of electricity generation while increasing the supply of cheap, reliable electricity?

The goal of this thesis is to conduct exergy and economic analyses of power plant systems that use coal and municipal solid wastes while minimizing the environmental impact from their combustion. The thesis will suggest ways to possibly have minimal environmental impact while generating positive rates of return on investment; however, it should be noted that the rates of return on investment of the power plant systems studied here are less than the rates of return using today's conventional natural gas and coal-fired power plants if there were no regulations on carbon dioxide emissions.

As such, it's important to discuss briefly why regulating carbon dioxide emission is crucial. While CO₂ is an essential species on our atmosphere, the problem is that humans and other species have adapted to living with concentrations of CO₂ near 300 ppm. Higher concentrations of CO₂ mean higher concentrations of greenhouse gases in the atmosphere and lower pH values for the ocean [2], since CO₂ is also a weak acid gas. In addition, when concentrations of CO₂ are above 1000 ppm [3], there can be health effects to long-term exposure to carbon dioxide [4][5]. It is this three-fold nature of CO₂induced problems that makes relatively simple solutions to the climate aspect of CO₂ impact, such as geo-engineering or adaptation, appear incomplete and unacceptable.

As for global warming, it is important to highlight

Exergy: is a thermodynamic variable that is always specified in reference to a given 'dead' state, such as the Earth's atmosphere. The exergy of a system is the maximum useful work that can be extracted during a process that brings the system into equilibrium with the environment, assuming that the environment is a reservoir in thermal, chemical and mechanical equilibrium.

The molar exergy of a control volume is defined as follows:

$$\hat{\varepsilon} = (\hat{h} - \hat{h}_0) - T_0(\hat{s} - \hat{s}_0) + \sum_i x_i (\hat{\mu}_i - \hat{\mu}_{i_0})$$

 \hat{h} is the molar enthalpy, T is the where temperature, \hat{s} is the molar entropy, x_i is the mol fraction of species *i*, and $\hat{\mu}$ is the chemical potential of species *i*. Terms without the naught symbol are for the system, and terms with the naught symbol are for the environment. The molar exergy can be greater or less than the first law definition of molar energy, which is typically defied as: $\hat{h} - \hat{h}_0$. While the difference between $\hat{\varepsilon}$ and $\hat{h} - \hat{h}_0$ for fuels like methane or carbon is only ~3%, the difference between $\hat{\varepsilon}$ and $\hat{h} - \hat{h}_0$ for low-grade forms of thermal energy can be ~100%. Further information on exergy can be found in the appendix of this thesis.

where there is uncertainty and where there is not a significant amount of uncertainty. CO_2 is a known greenhouse gas, which adsorbs in the infrared at a wavelength near 16 μ m [6]. While the peak at 16 μ m

is completely saturated, higher concentrations of CO_2 cause the wings of this peak to absorb more and more infrared radiation. There is virtually no uncertainty about the relationship between the concentration of CO_2 in the atmosphere and the change in the average radiative forcing on the Earth [6]. Chapter 2 of IPPC AR4: The Physical Science Basis gives a precise equation for converting a change in the concentration of CO_2 into a change in the "radiative forcing." The equation for the change in the radiative forcing is a constant times the logarithm of the ratio of the concentration in the current atmosphere:

$$\Delta F \text{ in } [W \cdot m^{-2}] = 5.35 \cdot ln(c/c_o)$$

One source of the uncertainty is in converting a change in radiative forcing into a change in the global average temperature. The IPCC stated in its 4th report that the climate sensitivity to a doubling of the CO₂ concentration would *"likely to be in the range 2 to 4.5°C with a best estimate of about 3°C* [6]." Another source of uncertainty is the uncertainty in converting a change of temperature into a change in social welfare. As of 2012 [7], fourteen research papers had been published which attempted to answer the question: what is the net economic impact of higher temperatures due to GHG emissions? The meta-analysis of 14 studies by Tol [8], as reproduced in Figure 1, suggests that there is a possible slight economic benefit from an increased temperature until a temperature increase of approximately 2.2 °C relative to 2009 global average temperatures.



Figure 1: Estimates of the global economic impact of climate change as a function of the rise of temperature. Data points reproduced from Tol [8]. Error bars, not shown, can be found in Tol [8].

After 2.5 °C, there appears to be a rapid increase in the economic damage associated with higher temperatures. Using this information and assuming a discount rate of 0%, 1% & 3%/yr, Tol [8] estimated that the mean economic damages per ton of CO₂ would be $63/tCO_2$, $23/tCO_2$, and $5/tCO_2$, respectively in 2009 dollars. So, even though there was short-term benefit to higher temperatures, due to the fact that CO₂ stays in the atmosphere for roughly 100 years, the long-term cost of emitting greenhouse gases was such that emitting a ton of CO₂ would have a net negative impact even assuming a 3%/yr discount rate. The net economic damage of CO₂ emissions is only expected to increase with time, because, as seen in Figure 1, CO₂ emitted in the future will likely cause more net damage than CO₂ emitted today, and because CO₂ concentrations would eventually become a health issue regardless of its impact on global temperatures or the pH of the oceans.

In this thesis, we focus on power plant designs that capture CO_2 and sequester it underground because the evidence appears to show that, in the long-run, higher CO2 concentrations will cause more harm than benefit. In chapter five of this thesis, we will step back and compare these power plant designs with power plant designs that do not capture CO_2 and we analyze cases for CO_2 emission taxes between \$0 and \$80/tCO₂.

1.2 Motivation for the Power Plant Systems Analyzed

Over the last decade, coal-fired power plants have generated approximately 40% of the total electricity across the globe [9]. In the United States, coal power plants supply approximately 40-50% of the demand for electricity [10]. For comparison, municipal solid waste power plants supply only approximately 0.3% of electricity demand [11]. Even the best designed pulverized coal power plants generate acid gases (NO_x, SO_x, and weakly CO₂), entrained particulates, and emit greenhouse gases (CO₂) at levels roughly twice as high as the U.S. EPA proposed regulations for new power plants. In 2012, the U.S. EPA proposed a set of regulations that would force the lifetime average emission of CO₂ from for new power plants to be less than 0.45 kg of CO₂ per gross kWh of electricity generated [12].

There are a number of different advanced coal power plant designs with CO₂ capture and sequestration (CCS) [13-19] that can meet the EPA requirement of greenhouse gas (GHG) emissions

[20]. These designs include the following general types [16]: (1) conventional pulverized coal combustion with CCS (PCC-CCS) using amine-based solvents for post-combustion capture; (2) conventional integrated gasification combined cycle with CCS (IGCC-CCS) using physical solvents operating near room temperature for pre-combustion capture; (3) advanced integrated gasification combined cycle with CCS (Adv. IGCC-CCS) using O₂ separation membranes as well as warm gas, pre-combustion capture of H₂S and CO₂; (4) oxy-combustion of coal or chemical looping combustion of coal using a transition metal redox cycle that generates a near pure stream of CO₂; and (5) chemical looping gasification using a calcium oxide-carbonate cycle in which a pure stream of CO₂ is generated in the calcination step [21-27]. There are unique advantages and disadvantages to each of these different configurations.

These coal-fueled power plant designs will be competing against each other and against natural gas, nuclear and storable renewable energies for a place in a competitive market for base load electricity. As such, there have already been a number of recent studies which have estimated the levelized cost of electricity from such carbon capture and sequestration (CCS) power plants [13-19, 28, 29]. In order to compare the economic viability of the power plant system configurations analyzed in this thesis, we will be using cost estimates from a number of these previous researchers [15, 30-33]. To make fair comparisons with previous research, we developed a consistent methodology so that the power plant configurations were analyzed using the same economic assumptions, such as the price of coal, discount rate, and operating & maintenance percentage costs.

While the calcium looping gasification process is not nearly as developed as the PC-CCS and IGCC-CCS processes, there are reasons why the calcium looping gasification process could achieve a lower LCOE than the conventional PC-CCS and IGCC-CCS processes. These reasons include the following: (1) the high methane content of the gas from the gasifier may allow for integration with existing natural gas combined cycle power plants [34, 35] while meeting proposed EPA regulations on GHG emissions; (2) there will likely be less equipment required because acid gas capture, methanation, and water-gas-shift all occur in the gasifier [36]; (3) the solid bleed-stream from this CaO-CaCO₃ process could likely generate revenue as a pre-calcined feedstock to cement kilns, potentially decreasing the GHG emissions of both power plants and cement kilns [21]; and (4) a CaO-CaCO₃ process should be fairly fuel flexible, being capable of handling fuels such as coal, biomass and municipal solid waste [37].

Chemical looping gasification of solid fuels with *in situ* capture of carbon dioxide, hydrogen sulfide, and hydrogen chloride provides a simple means of converting coal or municipal solid waste into a

gaseous fuel that is capable of being oxidized to generate electricity such that it can meet current and possible future regulations regarding both acid and greenhouse gas emissions. The gaseous fuel could be converted into synthetic natural gas (SNG). The gaseous fuel could also be sent to either the combustor of a gas turbine or to the anode of a high temperature fuel cell. Recent system studies [30, 31, 38] indicate that the system efficiencies of advanced fuel cell power plants can approach 60% while capturing >95% carbon dioxide, minimizing water consumption, and lowering the cost of electricity compared to pulverized coal combustion with carbon capture and sequestration (PCC-CCS) and integrated gasification combined cycle with CCS (IGCC-CCS) power plants. One of the keys to achieving this target is the production of a high methane synthesis gas (>20% dry vol. basis) in a coal gasifier that consumes little to no oxygen. This gasifier can operate without oxygen because the endothermic steam gasification reactions can be offset by the exothermic carbon dioxide capture and methanation reactions. Operating without oxygen enhances the cold gas efficiency of the gasifier, and the high methane content reduces the cooling load within the solid oxide fuel cell. By accomplishing what normally requires multiple distinct reactors and by eliminating the need for pure oxygen, a catalytic coal or waste gasifier with *in situ* carbon and sulfur capture has the potential to lower the cost of generating electricity and SNG while producing minimal to near zero emissions of acid and greenhouse gases. We now present an overview of topics covered in the thesis and how they pertain to producing electricity using fossil or waste fuels in ways that significantly lower the emission of greenhouse gases to the atmosphere.

1.3 Overview of Topics Covered

First, a molten catalytic process has been demonstrated for converting coal into a synthesis gas consisting of roughly 20% methane and 80% hydrogen using alkali hydroxides as both catalysts and *in situ* CO₂ capture agents. Baselines studies were also conducted using no catalyst, a weak capture agents (CaSiO₃) and strong *in situ* capture agents for acid gases (NaOH, KOH & CaO). Parametric studies were conducted to understand the effects of temperature, pressure, catalyst composition, steam flow rate and the coal-to-catalyst ratio on the performance of the molten catalytic gasifier in terms of kinetics and syngas composition.

Second, we present experimental results of coal gasification with and without the addition of calcium oxide and potassium hydroxide as dual-functioning catalyst-capture agents. Using two different coal types and temperatures between 700°C and 900°C, we studied the effect of these catalyst-capture agents on (1) the syngas composition, (2) CO₂ and H₂S capture, and (3) the steam-coal gasification kinetic rate. The syngas composition from the gasifier was roughly 20% methane, 70% hydrogen, and 10% other species when a CaO:C molar ratio of 0.5 was added. In addition, we conducted multi-cycle studies in which the CaCO₃ was calcined by heating to 900°C to regenerate the CaO, which was then reused in repeated CaO-CaCO₃ cycles. The increased steam-coal gasification kinetics rates for both CaO and CaO+KOH persisted even when the material was reused in six cycles of gasification and calcination. The ability of the CaO to capture carbon dioxide decreased roughly 2-3% per CaO-CaCO₃ cycle. We also discuss an important application of this combined gasifier-calciner to electricity generation and selling the purge-stream as a pre-calcined feedstock to a cement kiln. In this scenario, the amount of purge-stream required is fixed, not by the degradation in the capture ability, but rather by the requirements at the cement kiln on the amount of CaSO₄ and ash in the pre-calcined feedstock.

Third, we analyzed a power plant system that integrates a CaO-CaCO₃ chemical looping gasifier with a pressurized, solid oxide fuel cell (SOFC). We used the gas composition, steam-coal gasification rate and CO_2 capture cycle degradation rate from the previous chapter as input into the model of this CaO-looping gasifier. The pressurized solid oxide fuel cell (SOFC) was modeled based off of the Rolls Royce SOFC. The system generates three products: electricity, pre-calcined feedstock, and compressed carbon dioxide. Using capital costs estimates from a variety of sources, including Department of Energy cost estimates for fuel cell systems, we conducted an economic analysis of the system as a range of different operating pressures, current densities, fuel utilizations, and air stoichiometric ratios. We conducted a sensitivity analysis to determine the effect of changing some of the assumptions in our cost model, such as the price of the fuel cell system, the sale price of CO_2 , the sale price of electricity, and the fuel price.

Fourth, we present exergy and economic analyses of two advanced fossil fuel power plants configurations in which the CO_2 is captured outside of the gasifier: an integrated gasification combined cycle with advanced H_2 and O_2 membrane separation including CO_2 sequestration (Adv. IGCC-CCS) and an integrated gasification fuel cell cycle with a catalytic gasifier and a pressurized solid oxide fuel cell including CO_2 sequestration (Adv. IGFC-CCS). The goal of the exergy analysis was to evaluate the power generation and the exergy destruction of each of the major components. We estimated the capital, labor, and fuel costs of these power plants, and then calculated the internal rate of return on investment

(IRR) and the levelized cost of electricity (LCOE). In the Adv. IGFC-CCS case, we chose a configuration with anode gas recycle back to the gasifier, and then varied the SOFC pressure to find the optimal pressure under this particular configuration. One goal of this economic analysis was to compare the IRR and LCOE of the configurations analyzed above with the IRR and LCOE of other fossil fuel power plant configurations. For example, using capital/labor/maintenance cost estimates from the literature, we calculated the IRR and LCOE of conventional fossil fuel power plant configurations, including scenarios with CCS and scenarios with varying costs to emit CO₂. We also present results showing which power plant configuration yields the lowest value of LCOE as a function of the price of CO₂ emissions and a function of the price of natural gas, holding all other variables constant. Our calculations suggest that the Adv. IGCC and Adv. IGFC configurations analyzed are a promising way to significantly decrease the greenhouse gas emissions of both the electricity industry and the cement production industry while generating a supercritical fluid to aid in the enhanced oil recovery of underground petroleum products.

Finally, we applied SOFC and warm-gas clean-up models developed for these IGCC and IGFC power plants to the case of pressurized SOFC fueled with biogas produced from an anaerobic digester (AD). The generation of electricity at municipal wastewater treatment (WWT) plants presents a nearterm potential application for high temperature fuel cell systems. The scale of typical wastewater treatment plants treated corresponds well to the size of today's large-scale fuel cell systems (100 kW to 1 MW). Using recent cost estimates of AD's and sulfur removal equipment as well as DOE-SECA cost estimates for fuel cell systems, we performed parametric studies of the AD-SOFC system in order to minimize the normalized capital cost (\$/kW). The four independent variables were the current density, the stack pressure, the fuel utilization, and the total air stoichiometric ratio. We also compared the normalized capital costs of the AD-SOFC system with the normalized capital costs of two similar systems: an anaerobic digester integrated with an internal combustion engine (AD-ICE) and an anaerobic digester integrated with a micro gas turbine (AD-mGT) when the scale for these engines is on the order of 500 kW. Our calculations show that adding a new AD-SOFC system to an existing WWT plant can yield positives rates of return on investment, and can significantly outcompete other options for using biogas to generate electricity. AD-SOFC systems could convert WWT plants in net generators of electricity rather than net consumers of electricity while generating positives rates of return on investment.

Chapter 2 Catalytic coal gasification with *in situ* carbon and sulfur capture

2.1 Introduction

Reducing the pollution emitted by coal and MSW power plants in an economically viable manner and building power plants that co-generate fuels/chemicals during times of low electricity demand are pressing research goals for the electricity industry. One way to achieve both of these goals in an economically viable power plant is through the use of a catalytic gasifier that turns coal or waste into a methane-rich syngas. The methane-rich syngas then could be converted into pipeline quality natural gas, could be combusted on site in a gas turbine, or could directly generate electricity within a solid oxide fuel cell. In the fuel cell case, several research groups have shown that one can achieve overall system efficiencies near or above 60% on a higher heating value basis [30, 31, 38]. Methane in the syngas is crucial to achieving high system efficiency because internal reforming of the methane into hydrogen can reduce the parasitic loading that would be required to maintain the temperature of the SOFC [39, 40].

Conventional entrained flow gasifiers, such as Shell-Texaco gasifier, operate around 1400°C, produce little methane and are virtually free of any other hydrocarbons [41]. From an equilibrium thermodynamics point of view, the temperature of the gasifier must be lowered in order to increase the

composition of methane in the syngas. However, in order to maintain sufficient kinetics at these reduced temperatures, and hence to minimize gasifier costs, a catalyst is required [42]. Potassium carbonate, hydroxide, and sulfide were all found to catalyze both the steam-carbon reaction (C+H₂O \leftrightarrow CO+H₂) and the methanation reaction (CO + 3H₂ \leftrightarrow CH₄ + H₂O) [43-45]. The following are the main gasification reactions and capture reactions inside of the gasifier when the catalyst is alkali hydroxides, calcium carbonate, or calcium silicate. Also included are the changes in the Gibbs free energy between reactants and products for each reaction at 1000 K.

$$\begin{split} C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g) & \Delta H^{1000K} = +136 \text{ kJ/mol} & \Delta G^{1000K} = -8 \text{ kJ/mol} \\ CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) & \Delta H^{1000K} = -35 \text{ kJ/mol} & \Delta G^{1000K} = -3 \text{ kJ/mol} \\ CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g) & \Delta H^{1000K} = -225 \text{ kJ/mol} & \Delta G^{1000K} = +27 \text{ kJ/mol} \\ CO_2(g) + 2KOH(1) \leftrightarrow K_2CO_3(1) + H_2O(g) & \Delta H^{1000K} = -179 \text{ kJ/mol} & \Delta G^{1000K} = -220 \text{ kJ/mol} \\ CO_2(g) + CaO(s) \leftrightarrow CaCO_3(s) & \Delta H^{1000K} = -169 \text{ kJ/mol} & \Delta G^{1000K} = -23 \text{ kJ/mol} \\ CO_2(g) + CaSiO_3(s) \leftrightarrow CaCO_3(s) + SiO_2(s) & \Delta H^{1000K} = -78 \text{ kJ/mol} & \Delta G^{1000K} = +68 \text{ kJ/mol} \\ \end{split}$$

Yeboah et al. [46] and Sheth et al. [47] have studied the effect of different catalysts on the gasification rate, and found that mixtures of alkali species (lithium, sodium, potassium, and rubidium) are most effective when the anion is a weak acid, such as $CO_3^{2^-}$ or OH^- , as opposed to a strong acid, such Cl. The methods of the Exxon catalytic coal gasification process [48] were to operate at lower temperatures than conventional gasifiers, to impregnate coal with 20%wt K₂CO₃ as a catalyst, and to react the coal with steam and recycled syngas (H₂, CO) in a single-stage, fluidized-bed gasifier. The goal was to produce a syngas with high methane and CO₂ concentrations. The gasifier operated at roughly 700°C and 3.5 MPa [49]. It should be noted that 20%wt K₂CO₃ represents approximately 5% potassium compared to the carbon in the coal on a molar basis, and we will present results using potassium carbonate at this same ratio. CO₂ was captured downstream of the gasifier, and methane was separated cryogenically from the remaining H₂ and CO, which was recycled back to the catalytic gasifier. Calcium hydroxide was used in a digestion process to yield about 90% catalyst recovery from the char/ash. The overall carbon conversion was roughly 90%, producing mainly methane and CO₂ as end products. To the best of our knowledge, the Exxon catalytic coal gasification process did not reach commercial scale, and was only demonstrated at the pilot-plant scale [48]. A similar process is currently being commercialized by GreatPoint Energy [50].

Instead of using alkali carbonates, another well studied coal gasification catalyst is calcium oxide. Calcium oxide acts as both a gasification catalyst and as a capture agent for acid gases, such as H₂S and CO₂. Calcium oxide has been a well-studied coal gasification catalyst because of the abundance of calcium carbonate. The use of CaO to aid in the gasification of coal was first patented in 1867 [51]. Carbon dioxide capture and regeneration by calcium oxide has been studied and reviewed by many previous groups, such as Stamnore and Gilot [52], Florin and Harris [53], Liu et al. [54] and Dean et al. [21]. While CaO can capture HCl, H₂S and CO₂, only CO₂ can easily be regenerated by increasing the temperature and/or decreasing the pressure. Gasification processes using calcium oxide addition have typically been studied when there has been a need to produce a syngas with high methane or hydrogen content. For example, the goal of the CaO acceptor process by Consol Energy in the 1960s-1980s [22] was to generate a high content of methane and a low content of carbon dioxide. The goal of more recent chemical looping fluidized bed gasifiers, such as the HyPr- RING [23] and the calcium looping process (CLP) [24-26], has typically been to generate a near pure stream of hydrogen. The HyPr – RING process is a pilot plant scale reactor system, whose gasification reactor operates at 650°C, 3.0 MPa, and a molar CaO/Carbon ratio of ~0.8 while generating a syngas of roughly a 91% H₂ and 9% CH₄, on a dry molar basis. The calcium looping process (CLP) at the Ohio State University [24-27] is a two-fluidized-bed reactor process whose goal is to generate near-pure hydrogen. One advantage of calcium oxide as a catalyst is that it remains in the solid phase and would not strongly interact with either the ceramic or the steel walls of a gasifier. Though, the fact that lime and limestone are solids at typical gasifier temperatures is part of the reason that they are not as good catalysts as alkali catalysts.

One way of achieving fast kinetics is to operate with a molten bed of catalysts, such as molten alkali carbonates or hydroxides, which provide for high mass and heat transfer. Previous research into molten bed gasification includes research by Kellogg and Rockwell International [55-58] in the 1970s as well as recent research by Tokyo Institute and Nagoya University [59, 60]. At the time that most of the original research on catalytic gasification was conducted, reducing CO_2 emission was not a driving force for the research, and it has not been until relatively recently that research has been published on molten beds of alkali hydroxides specifically for *in situ* CO_2 capture. Kamo *et al.*[61] used alkali hydroxides to capture CO_2 and HCl while producing relatively pure hydrogen from a chlorine-containing waste plastic. The molten bed designed by Kamo *et al.*[61] was ideal for generating hydrogen because the pressure was near atmospheric and there is an excess of alkali hydroxides. By using an excess of alkali hydroxides,

Kamo *et al.*[61] were able to maintain a molten bed, even though the gasifier temperature was below the melting point of sodium and potassium carbonate.

One goal of the research in this thesis was to experimentally operate a molten alkali gasifier so as to obtain high concentrations of hydrocarbons and high kinetic rates of gasification. The gasifier was operated at moderate temperatures ($600^{\circ}C - 900^{\circ}C$) and elevated pressures (2.1 MPa). In addition, on a per carbon basis, less alkali hydroxides and water vapor were sent to the gasifier than in the molten alkali hydroxide gasifier operated by Kamo *et al.* [61]. This means that we expect most of the alkali hydroxide to convert to alkali carbonates. In order to maintain the bed in a molten state, we used an equimolar mixture of LiOH, NaOH, and KOH. For example, the melting point of a near equal mixture of lithium, sodium and potassium carbonate is roughly $400^{\circ}C$ [46], which means that the molten alkali species should remain molten even after capturing carbon dioxide. As in the work by Kamo *et al.* [61], the alkali hydroxides not only catalyze the steam-coal gasification reaction; they can also capture acid gases, such as HCl, H₂S, and CO₂, inside of the gasifier. The alkali hydroxides can be regenerated from these alkali chlorides, sulfides and carbonates outside of the gasifier using cation-selective polymer membranes [62-64], such as Nafion®.

However, given the necessary exergy destruction of cooling the alkali carbonates to aqueous temperatures required for such electrodialysis methods, we chose to use CaO as the main capture agent in a series of cyclic experiments of CO_2 capture inside the gasifier and regeneration of CaO in a calciner. We will demonstrate that a catalytic gasifier using CaO and alkali hydroxides is a potentially viable means of converting coal or municipal solid wastes into a syngas with the potential to generate synthetic natural gas or electricity with minimal to near zero emissions of acid gases, greenhouse gases, and particulates.

2.2 Experimental Set Up

2.2.1 Materials

The chemicals used as catalysts were obtained from Alfa Aesar (Ward Hill, MA) and the coal samples were obtained from the Argonne National Laboratory Premium Coal Bank [65], whose website contains

the full information on the coals used, such as particle distribution, elemental analysis and proximate analysis. We used 5 g dry samples of a high volatile bituminous coal (Pittsburgh#8 100 mesh) as well as sub-bituminous coal (Wyodak-Anderson 100 mesh). These two coals represent the two main types of non-lignite, coals used in the US: a medium-sulfur Eastern bituminous coal and a low-sulfur Western, sub-bituminous coal. Table 1 lists the coal composition on a weight basis as well as the molar, ash-free composition of the coal and the weight composition of the ash.

Table 1: Main components of the Pittsburgh#8 bituminous coal and Wyodak-Anderson sub bituminous coal. Data from the ANL Premium Coal Bank.

Coal	C [% wt]	H [% wt]	O [% wt]	N [% wt]	Total S [% wt]	Ash [% wt]	
Pittsburgh#8	73.1	4.7	7.8	1.5	2.2	9.1	
Wyodak-Anderson	68.3	4.9	16.4	1.0	0.6	8.8	
	С	Н	0	Ν	Org S		
	[% mol]						
Pittsburgh#8	53.5	41.1	4.3	0.9	0.2		
Wyodak-Anderson	48.8	41.7	8.8	0.6	0.1		

(a) Dry weight percentage and dry, non-ash elemental percentage

(b)	Ash	composition	on a	weight	percentage
$\langle \sim \rangle$		eon position	· · · ·		PB-

Coal	Na2O+K2O [% wt]	CaO [% wt]	MgO [% wt]	BaO+SrO [% wt]	Fe2O3 [% wt]	Al2O3 [% wt]	TiO2 [% wt]	SiO2 [% wt]	P2O5 [% wt]	SO3 [% wt]
Pitt#8	2.1	2.6	1.3	0.0	19.5	25.2	1.2	45.9	0.0	2.0
W-A	2.3	15.1	3.6	0.9	10.2	15.5	1.2	28.7	1.2	22.0

In most of the experiments, fresh coal was used; however, we also present results for pyrolyzed Pittsburgh#8 coal. In that case, de-volatilization of coal was performed at 700°C for 4 hours in an argon atmosphere. After de-volatilization, the coal was ground and sieved to 20 mesh size. The de-volatilized coal was then mixed with the catalyst, and de-volatilized a second time under an argon atmosphere at 700°C before steam was introduced into the reactor. The de-volatilization was done to determine the syngas composition excluding pyrolysis gases, and hence to quantify the non-pyrolysis methane production as a function of pressure.

We focus mostly on the Wyodak-Anderson coal from Wyoming because its low-ash, low-sulfur, and high reactivity make it an ideal fuel for low-temperature, calcium oxide looping gasification. The sulfur

in the Wyodak-Anderson coal is 27% wt pyritic (FeS₂), 5% wt, sulfatic (SO₄⁻²), and 68% wt organic (C-H-O-N-S). The sulfur in the Pittsburgh#8 coal is 63% wt pyritic and 37% wt organic. As for a dry proximate analysis, in the Wyodak-Anderson coal is 45% wt volatile matter and the Pittsburgh#8 coal is 38% wt volatile matter. The ash composition of the coal is shown in Table 1(b) on a weight basis, with basic ash components on the left and acidic components on the right. The Pittsburgh#8 coal is predominantly composed of silica, alumina and iron oxide. The Wyodak-Anderson coal also has significant amounts of CaO and SO₃.

2.2.2 Reactor design

A pressure vessel was constructed that could withstand relatively high temperatures, high pressures, and alkaline conditions. The reactor system and associated equipment are shown in Figure 2. The reactor system was placed inside of a Series 3110 Tube Furnace by Applied Test Systems (Butler, PA). The main piece of equipment was a pressure vessel constructed out of Incoloy® 800HT, and with a ceramic crucible at the bottom that holds the mixture of catalyst and coal. A tube carrying steam was placed inside of the ceramic crucible, such that the steam has to pass through a molten bed of coal and catalyst. A thermocouple was placed inside of the molten bed, which was used to control the furnace. The dimensions of the 99.8% pure, alumina crucible (CoorsTek, Golden, CO) inside of the reactor were: 23 cm tall (9"), 2.5 cm outer diameter (1"), and 1.9 cm inner diameter (0.75"). The steam tube was 1.3 cm ($\frac{1}{2}$ ") 316 stainless steel tubing.

After the syngas exits the reactor, the syngas was cooled in a water bath so that liquids would condense before going through a pressure controller. Species that can condense from the syngas include water and tars, and depending on the pH of the liquids in the condenser, species such as ammonia, hydrogen sulfide and carbon dioxide can also condense out before the back pressure controller. All experiments were semi-continuous, meaning that there was a set amount of coal and catalyst loaded into the reactor and then there was a continuous flow of steam into the reactor. So, by the end of each experiment, the coal was mostly consumed, and the main gas specie in the pre-quenched syngas was just the water vapor being continuously added.

Our experiments included several parametric studies, in which we varied: (1) catalyst type, (2) reactor temperature, (3) catalyst-to-coal ratio, (4) steam-to-coal ratio, and (5) reactor pressure. The catalysts used were the following: (1) an equimolar mixture of LiOH : NaOH : KOH, (2) K_2CO_3 , (3) CaO, (4)

CaO+KOH, and (4) CaSiO₃. In case (1), we used an equal mixture of alkali hydroxides, rather than just sodium or potassium hydroxide, so that the melting point of alkali carbonates was less than the temperature within the gasifier.



Fig. 2. Catalytic gasification reactor design. Steam and coal react in a bed of catalysts. (a) Experimental set up (b) Schematic and zoom-in of reactor system (c) Process flow diagram.

The range of values and the standard values for operating conditions are listed Table 2. An alkali to carbon ratio of 1 means that the total number of moles for alkali species is equal to the number of moles of carbon in the coal. Since equi-molar amounts of Li, Na, and K were used, this means the ratio of elements on a mole-basis was C:Li:Na:K = 3:1:1:1, for most cases examined here. It should be noted that a water flow rate of 0.05 g/min corresponds to a flow rate of 0.56 mol H₂O/mol-C/hr, which means
that each hour roughly half of a mole of water is added to the reactor for every mole of original carbon in the reactor. This molar flow rate of water vapor (62 sccm) into the reactor was six times larger than the flow rate of argon (10 sccm). The diffusivity of water vapor in the reactor was over three orders of magnitude larger than the gasification reaction rates, and hence the water vapor composition within the reactor should be spatially constant, even though it will be changing with time as amount of coal remaining decreases with time.

	Range of values	Nominal value
Pressure [MPa]	0.1 - 2.1	2.1
Temperature [°C]	600 <u>900</u>	700
Catalyst to carbon ratio [-]	0 _ 2	0.5
Water flow rate [mL/min]	0 _ 0.1	0.05

Table 2: Range of values and standard values of process variables

We now discuss the experimental procedures. Before loading the ceramic crucible, the fresh coal and catalyst were mixed together dry outside of the crucible. Next, the stainless steel steam tube was inserted into the ceramic crucible. The dry, mixed catalyst and coal were poured inside of the ceramic crucible, outside of the steam tube. For those cases in which there was the addition of water, we then added 30 g of deionized water and mixed the coal and catalyst inside of the ceramic crucible. The crucible was then placed inside of the Incoloy® 800HT reactor, and finally the system was sealed. For those cases with water addition, the water was evaporated before the experiment began by heating the system to 200°C. For those cases in which the catalyst was reused for a number of cycles, the material from the previous run was removed from the ceramic crucible after allowing the reactor to cool back to room temperature. The material was weighed in order to make sure that all material had been recovered. The weight was always within $\pm 5\%$ of the expected weight due to the previous material plus the new ash material in the coal added in the previous experiment. During cool down, dry air was passed over the bed of CaO in order to prevent the formation of Ca(OH)₂. We did not see a significant change in the weight of the CaO, even when exposed to room air. After collecting the catalyst and ash material from the previous run, we ground the material until all of the material passed through a 20 mesh sieve (841 µm size opening.)

2.2.3 Product analysis: Gas composition and flow rate

In this section, we detail the process for how we converted the syngas composition versus time data from the mass spectrometer into a time-averaged gas composition. After liquids were condensed and the pressure was reduced, the syngas composition was measured using a mass spectrometer (Pfeiffer OmniStar, Asslar, Germany). Occasionally, the syngas was sampled just before the pressure controller and analyzed using gas chromatography to validate results from the mass spectrometer. The composition of water vapor in the syngas could not be measured because a condenser was placed before both the mass spectrometer and the sample port for the gas chromatograph. The mass spectrometer was calibrated using a series of known binary gas mixtures as well as a gas mixture with the following composition: 60% H₂, 20% CH₄, 10% Ar, 5%CO₂, 2% CO, 2% N₂, 1% C₂H₆, and 0.5% C₂H₄. The results from the mass spectrometer were also validated by steam-graphite gasification. Steam-graphite gasification is the following:

$$\dot{n}_{H_2} = \dot{n}_{C0} + 2 \cdot \dot{n}_{C0_2} - 2 \cdot \dot{n}_{CH_4} - 3.5 \cdot \dot{n}_{C_2H_6} \tag{1}$$

where \dot{n}_i is the flow rate of species, *i*. This equation was verified during baseline testing by steamgasifying graphite at 900°C, 2.1 MPa, and measuring an average dry syngas composition of 64% H₂, 31% CO₂, 4% CO, 0.6% CH₄, and 0.2% C₂H₆.

The real-time gas composition data from the mass spectrometer was converted into a productionaveraged gas composition through the following procedures: (1) determine the flow rate of each component of the syngas by multiplying the known inlet flow rate of argon by the ratio of the gas composition of the syngas species to the gas composition of the argon; (2) integrate the flow rate of each syngas species from the start of the reaction until 60% coal conversion; and finally, (3) divide the total flow of each gas species by the total non-argon gas flow. The equation for the production average gas composition, $PAGC_i$, of the syngas species *i* is given by the following:

$$PAGC_{i}(t) = \frac{\int_{0}^{t} \dot{n}_{Ar} \cdot \left(\frac{c_{i}(t)}{c_{Ar}(t)}\right) dt}{\sum_{i} \int_{0}^{t} \dot{n}_{Ar} \cdot \left(\frac{c_{i}(t)}{c_{Ar}(t)}\right) dt}$$
(2)

where \dot{n}_{Ar} is the flow rate of argon, $c_i(t)$ is the concentration of species *i* at a particular time, *t*. We chose 10 sccm of argon as the inert gas flow rate so that the vessel volume was never more than 20% inert gases. This way, there was never a significant difference in syngas partial pressure when operating at the same overall pressure if no inert gases were present. The values of pressure given throughout this work are the total pressure of gases in the reactor, including water vapor and argon. We chose to use argon, rather than nitrogen, as the known inert gas because there are no overlaps in the mass spectrometer analysis between argon and any of the syngas species of interest. At each value of temperature, pressure, catalyst-to-coal ratio, we ran three experiments and calculated the mean gas composition from the three realizations. The following section explains how we determined the cumulative coal conversion.

2.2.4 Product analysis: Reaction kinetics via reduction charge balance

It is not possible to do a real-time, elemental balance for this reactor because (a) there was carbon and sulfur capture by the catalysts and (b) water vapor was condensed before the mass spectrometer. However, the species that were captured or could not be measured, such as CO₂ and water, have no chemical oxygen demand [66]. In order to measure the amount of coal conversion and hence the rate of coal conversion, we generalize the concept of chemical oxygen demand into the concept of reduction charge remaining, where 'reduction charge' is defined as the number of electrons that can be generated at the anode of a hypothetical fuel cell when oxygen is used as the oxidant in the cathode. The reduction charge, which is given in units of [mol e⁻], is equal to four times the chemical oxygen demand (COD) when the COD is given in units of $[mol O_2]$. The concept of chemical oxygen demand in units of $[g O_2/$ L] is often used in wastewater treatment plants to estimate the amount of combustible material in wastewater [67]; however, the concept of chemical oxygen demand is rarely used in research papers on coal/biomass gasification or fuel reforming. While Berguerand et al. [68] used the concept of 'oxygen demand' to estimate carbon conversion in a chemical looping combustor, most gasification or fuel reforming studies measure coal conversion either through a mass balance [69] or carbon balance [70]. Instead of using a mass balance or a carbon balance, coal conversion can be measured by measuring the flow rate of those gas species exiting the reactor and assigning values to each gas species according to the mol e⁻ of charge that can be generated at the anode of a hypothetical fuel cell, i.e. by measuring the chemical oxygen demand of the syngas leaving the reactor.

Reduction charge remaining provides a better definition for coal conversion than conversion of coal

by mass because there is no one-to-one correspondence between the mass of the elements in coal and their reduction charge. For example, light species like hydrogen can volatilize from coal without a significant change in mass of the coal, but can cause a significant measurable change in the chemical oxygen demand of the remaining coal. Whereas heavy species like carbon dioxide can volatilize from coal with a measurable change in the mass of the coal, but without a significant change in the chemical oxygen demand of the remaining coal. In our case, we measure coal conversion by measuring those species exiting the reactor that have a reduction charge, such as H₂, CO, CH₄, C₂H₄, and C₂H₆. Also, since there is no oxygen in these experiments, there is conservation of reduction charge in our experiments, i.e. the total reduction charge of the exiting syngas is exactly equal to the reduction charge of the original coal. Though, it should be noted that the concept of reduction charge balance is generic enough that it could account for oxygen addition into a gasifier, a combustor, or a fuel reformer.

For each element in the coal or catalyst, the following values were assigned: C = +4, H = +1, O = -2, N = 0, S = -2, Ar = 0, Li, Na, K = +1, and Ca = +2. The value of reduction charge for the gas species measured by the mass spectrometer were the following: $H_2 = 2$, CO = 2, $CO_2 = 0$, $CH_4 = 8$, and $C_2H_6 =$ 14. If molecular oxygen had been added, it would have been assigned a value of $O_2 = -4$. Using the same elemental values above, we also calculated the value of reduction charge for the solid-state phase species in the gasifier: $CaO = CaCO_3 = CaS = KOH = K_2S = K_2CO_3 = 0$. The values of reduction charge listed above are the values for the number of electrons generated or consumed on an electrode of a hypothetical fuel cell. For example, graphite (C) can generate 4 electrons; anthracene ($C_{14}H_{10}$) can generate 66 electrons; methanol (CH₃OH) can generate 6 electrons; and ammonia (NH₃) can generate 3 electrons. As mentioned earlier, the value of reduction charge is equal to 4 times the value of the chemical oxygen demand. Note that we have assigned a reduction charge value of -2 for sulfur; however, the correct value should actually be +6 because the end redox state of sulfur in the environment is $SO_3(g)$ and $H_2SO_4(a)$. However, inside a gasifier, the final redox state of sulfur is -2 (i.e. Na₂S, H₂S). Sulfur is the last of the main coal species oxidized under partial oxidation. For this reason, we have decided to assign a reduction charge value of -2 to sulfur. This means that the capture of $CO_2(g)$, COS(g) or $H_2S(g)$ has no effect on the reduction charge (i.e. chemical oxygen demand) of the syngas, and hence has no effect on the calculation of coal conversion.

A general conservation equation can be written for the reduction charge:

$$\frac{\partial (RCR)_{System}}{\partial t} = \sum_{i}^{Inlet} \widehat{RC}_{i} \cdot \dot{n}_{i} - \sum_{j}^{Exit} \widehat{RC}_{j} \cdot \dot{n}_{j}$$
(3)

Where RCR is the reduction charge remaining, \widehat{RC} is the molar reduction charge, and \dot{n} is the flow rate of species entering or exiting the system. For our system, this equation reduces to the following:

$$\frac{\partial (RCR)_{Coal}}{\partial t} = -\left(2 \cdot \dot{n}_{H_2} + 2 \cdot \dot{n}_{CO} + 8 \cdot \dot{n}_{CH_4} + 14 \cdot \dot{n}_{C_2H_6}\right) \tag{4}$$

Note that the reduction charge of the system is equal to the reduction charge of coal because the catalysts and any gas species captured by the catalyst have a net reduction charge of zero. Also, there is no reduction charge flowing into the system because the only inputs are water vapor and argon.

Using the elemental analysis presented earlier in Table 1, each 5 g sample of dry Pittsburgh #8 coal contains 0.31 mol of C, 0.25 mol of H, 0.025 mol of O, 0.005 mol of N, and 0.003 mol of S. By assigning a reduction charge value, as listed above, to each element in the coal, we obtain a value of 1.43 mol e⁻ for every 5 g of Pittsburgh#8 coal. Each 5 g sample of dry Wyodak-Anderson coal contains 0.29 mol of C, 0.25 mol of H, 0.05 mol of O, 0.004 mol of N, and 0.001 mol of S. This yields a value of 1.31 mol e⁻ of reduction charge for every 5 g of dry Wyodak-Anderson coal.

To determine the percentage of coal remaining as a function of time, we first converted the flow rate of each gas species from units of sccm to mol e⁻ by using its assigned value of reduction charge. We then integrated the flow rate of reduction charge leaving the reactor from t=0 to t=t for all values of t. The normalized reduction charge remaining (NRCR) of the coal as a function of time for our batch reactor is defined as follows:

$$NRCR(t) = 1 - \frac{\int_0^t (2 \cdot \dot{n}_{H_2} + 2 \cdot \dot{n}_{CO} + 8 \cdot \dot{n}_{CH_4} + 14 \cdot \dot{n}_{C_2H_6})dt}{4 \cdot n_C + 1 \cdot n_H - 2 \cdot n_O + 0 \cdot n_N - 2 \cdot n_S}$$
(5)

The NRCR is also equal to the normalized chemical oxygen demand remaining (NCODR), which can be defined as follows:

NCODR(t) =
$$1 - \frac{\int_0^t (\frac{1}{2} \dot{n}_{H_2} + \frac{1}{2} \dot{n}_{CO} + 2 \dot{n}_{CH_4} + 3.5 \dot{n}_{C_2H_6})dt}{n_C + \frac{1}{4} n_H - \frac{1}{2} n_O + 0 \cdot n_N - \frac{1}{2} n_S}$$
 (6)

In order to determine the first order rate constant, we plotted the NRCR as a function of time and fit an exponential curve to the data up to 60% conversion, i.e. when the NRCR equals 40%. Note that, if the rate constant were purely first order throughout the experiment, then we would not have to specify a rate constant to 60% conversion. However, as will be seen in the results section, the rate constant for up to 60% conversion is larger than the rate constant through the entire run because of the significant amount of volatilization early in the experiment. We chose the value of 60% conversion because this was the largest value of conversion reached by all data sets. While some data sets with alkali hydroxides reached conversion values as high as 99% conversion, many of the data sets without catalyst reached 60% conversion only after 300 minutes of operation.

2.2.5 CaO regeneration and calculation of CO₂ captured

In this section, we detail the process for how we converted the data from the mass spectrometer during the regeneration (i.e. calcination) step of the cycle into both a kinetic rate of CO₂ desorption as well as a value for the total desorption of CO2. After each regeneration/calcination, the material was removed from the ceramic crucible and mixed with the fresh coal before being added back into the reactor. There was no addition of fresh CaO into the process after the beginning of Cycle#1. After each gasification experiment with CaO, the following steps occurred: the flow rate of steam was turned off; the pressure was released back to 0.1MPa; and the reactor temperature was raised to 900 °C. It took roughly 20 minutes for the temperature to go from 700°C to 900 °C. During the CO₂ desorption phase of the CaO-CaCO₃ cycle, we maintained the same flow of argon (10 sccm) as in the gasification phase. After 90 minutes of calcination, 200 sccm of air was added for an additional 30 min. While this does not represent what would occur at a commercial facility, we followed this procedure in order first study the release of CO₂ from the calcium carbonate in the absence of oxygen so that we could directly measure CO_2 release from the calcium carbonate rather than having to separate this amount from the amount of CO_2 generated via combustion of the remaining coal. To measure the flow rate of CO_2 released from the calcium carbonate, we multiplied the argon flow rate (10 sccm) by the ratio of the CO₂ gas composition to the argon composition plus one half the ratio of CO gas composition to the argon composition. We counted half of the carbon monoxide composition towards the carbon dioxide release because some carbon dioxide reacts via the reverse Boudouard reaction with any unburnt carbon in the coal since this reaction is spontaneous at temperatures above 700 °C. The reverse Boudouard reaction, $C(s) + CO_2(g)$

 $\rightarrow 2$ CO(g), is spontaneous at the temperature of calcination ($\Delta G^{1173K} = -40 \text{ kJ} \cdot \text{mol}^{-1}$), and therefore, we had to count half of the CO generated during this desorption phase towards the total CO₂ released from the calcium carbonate. To calculate the total CO₂ released, we integrated the molar flow rates with respect to time to determine the total moles of CO₂ released. Finally, to measure a normalized amount of CO₂ released, we divided this integral by the total moles of CaO added to the gasifier. The equation is given below:

$$NCP(Method \#1) = \frac{\int_{t'}^{t'+90\,min} (\dot{n}_{CO_2} + 1/2 \cdot \dot{n}_{CO})dt}{n_{CaO}}$$
(5)

where *NCP* is the normalized capture percentage, t' represents the time at which gasification ends and calcination begins, \dot{n}_i is the molar flow of species *i*, and n_{CaO} is the moles of CaO added to the gasifier at the start of the experiment. It should be noted here that the kinetic rate for CO₂ calcination was on the order of 3 hr⁻¹, so 90 minutes of calcination represents roughly 4.5 e-folding decay times, and hence only 2% or less of the CO₂ would not have been released by the end of 90 minutes.

We also compared the values of NCP calculated in this method with an estimate of the CO_2 captured during the steam-coal gasification portion of the experiment. To estimate the amount of CO_2 capture, we subtracted the amount of carbon that leaves the reactor during coal gasification (i.e. the amount of $CH_4+CO+CO_2+2\cdot C_2HC$) from the amount of carbon in the coal that reacts during gasification.

$$NCP(Method \# 2) = \frac{(1 - NCRC) \cdot n_C - \int_0^{t'} (\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4} + 2 \cdot \dot{n}_{C_2H_6} + 2 \cdot \dot{n}_{C_2H_4}) dt}{n_{CaO}}$$
(5)

where *NCRC* is the normalized coal remaining at the end of gasification, n_c is the moles of carbon in the 5.0 g of coal added at the beginning of the experiment. It should be noted that method#2 is less exact because it assumes that C, H, and O atoms are gasified at the same rate.

These two methods of calculating the normalized capture percentage provide a verification of our estimates of how much CO_2 was captured during gasification. The values of normalized capture percentage presented in sections 3.5 and 3.6 are the average of the " CO_2 captured" and the " CO_2 released", as estimated by the two methods discussed above. These calculations allow us to measure the amount of CO_2 captured during the gasification phase of each experiment, and allows us to measure the degradation in the capture ability after repeated CaO-CaCO₃ cycles.

While it was not possible to conduct a carbon balance for just the gasification portion of this experiment, we were able to conduct an overall carbon balance analysis across the combined gasification and calcination portions of the experiment. In the results section, we will be including the carbon balance, which is defined as the total carbon exiting the reactor during the entire experiment normalized by the carbon originally in the coal. The average measured carbon balance across the 12 experiments shown later in Table 14 was 96% and the standard deviation was 10%, which means that the expected value for the carbon balance (100%) falls within 1 standard deviation of the average measured value for the carbon balance.

2.3 Results

The experimental results are presented in the following order: gasification results during start-up (Sections 2.3.1); gasification results vs. time after start-up (Sections 2.3.2); effect of catalyst type (Sections 2.3.3); effect of temperature without and with catalyst (Sections 2.3.4-7); effect of catalyst-to-coal ratio using molten alkali hydroxides (Sections 2.3.8); effect of steam-to-coal ratio using molten alkali hydroxides (Sections 2.3.9); effect of pressure using molten alkali hydroxides (Sections 2.3.10); and, finally, gasification results vs. cycle number using CaO or CaO+KOH (Sections 2.3.11-12).

2.3.1 Results during the start-up phase

Here, we present gas composition and coal conversion during the start-up phase of experiments with and without catalyst addition in order to measure the amount of pyrolysis occurring during start-up. These data will be presented as a function of the temperature inside the reactor. Since the temperature inside the reactor increased at an average rate of 11°C per minute, the results can easily be converted into results versus time. First, we present in Figure 3 (a) the gas composition and coal conversion during the start-up phase when there was no steam flowing and no catalyst added with the Wyodak-Anderson coal. Any gas produced during start-up is therefore only due to de-volatilization reactions (i.e. pyrolysis) or subsequent reaction of released carbon dioxide with the coal to form carbon monoxide. During the start-up with no steam and no catalyst, approximately 2% of the coal's reduction charge exits the reactor. The first gas to be released was carbon dioxide, and this process began around 350° C. Then at 400° C, there was release of carbon monoxide, methane, ethane/ethylene, and hydrogen. The timing of the release of these pyrolysis gases is similar to the timing found by Wen and Dutta [71], who found that volatile species typically are released from the coal in the following order: H₂O, CO₂, CO, C₂H₆, CH₄, tars/liquids, and H₂. The CO₂ released comes from decarboxylation of the carboxyl acid groups in the coal. While on a molar basis carbon dioxide and carbon monoxide are the dominant pyrolysis gases, on a reduction charge basis, methane is the dominant species in the pyrolysis gas because the carbon dioxide that exits the reactor has no reduction charge. When the temperature reaches 700°C, methane makes up roughly 75% of the reduction charge leaving the reactor.





Figure 3: Gas composition and normalized coal conversion (NCC) during the temperature ramping start- up for 5.0 g of Wyodak-Anderson coal. The reactor volume was initially just solid coal and 100% Ar. (a) No steam and no catalyst, (b) continuous flow of 0.05 g·min⁻¹ of water plus 8.2 g of CaO mixed with coal before start-up, (c) continuous flow of 0.05 g·min⁻¹ of water plus 8.2 g of CaO and 1 g of KOH mixed with 30 g of water and coal before start-up, and (d) continuous flow of 0.05 g·min⁻¹ of water 2.5 g of LiOH, 4.2 g of NaOH, and 5.9 g of KOH. Note the different scales for each axis (Right hand side y-axis scale for NCC only). The temperature increase inside of the reactor was approximately linear with a ramp rate of 11°C·min⁻¹.

In Figure 3 (b), we present the gas composition and coal conversion during the start-up phase of an experiment with 5.0 g of Wyodak-Anderson coal, 8.2 g of CaO, 62 sccm steam flow, and 10 sccm of argon flow. The reactor volume was initially just solid coal and 100% Ar until roughly 500°C. There is no noticeable increase in the composition of carbon dioxide at 350° C or carbon monoxide at 400° C. It is possible that the CaO was capturing the carbon dioxide and preventing the carbon dioxide gas from reacting with the coal to form carbon monoxide. The presence of steam as well as 0.5 mole of CaO per mole of carbon in the coal causes the gas composition to be very different in these first two cases. When there was no calcium oxide and steam, the gas had large quantities of carbon dioxide; however, when there was calcium oxide and steam, the gas composition was mostly hydrogen and methane. As seen in Figure 3 (b), at 650°C there was a rapid increase in the composition of hydrogen, which was generated by a combination of steam-coal gasification, water-gas-shift, and pyrolysis reactions. But by 700°C in both Figure 3 (a) and (b), roughly the same amount of reduction charge had left the reaction during the start-up phase of the experiment. This suggests that the CaO does not speed up the pyrolysis reactions, and suggests that the effect of the CaO is to capture CO₂ and H₂.

In Figure 3 (c), we present the gas composition and coal conversion during the start-up phase of an experiment with 5.0 g of Wyodak-Anderson coal, 8.2 g of CaO, 1 g of KOH with a continuous flow of 62 sccm of steam and 10 sccm of argon. The reactor volume was initially just solid coal and 100% Ar until roughly 300° C. In Figure 3 (c), we can see the clear positive effect of mixing the coal, catalyst, and water. In all twelve experiments conducted with CaO/KOH and water, there is hydrogen production at temperatures at least 100° C lower than for the pyrolysis case or the case of adding calcium oxide that has only been dry mixed with the coal. Similar to the case with just CaO addition, there was virtually no CO₂ in the start-up gas stream. By 600° C, 9% of the reduction charge had already been released and we had to define the start of the gasification phase to be equal to when the reactor reached 600° C, rather than the normal definition of the start for the start of gasification phase as when the reactor reaches 700° C.

In Figure 3 (d), we present the gas composition and coal conversion during the start-up phase of an experiment with 5.0 g of Wyodak-Anderson coal, 2.5 g of LiOH, 4.2 g of NaOH, and 5.9 g of KOH with a continuous flow of 62 sccm of steam. In this case of using a mixture of molten alkali hydroxides, the production of hydrogen began around 400 $^{\circ}$ C, which was similar to case 4(c). Also similar to the cases of using CaO as the capture agent (b-c), there was virtually no CO₂ exiting the gasifier during start-up.

2.3.2 Gasification with and without catalyst

Here, we present the flow rate and normalized reduction charge remaining (NRCR) versus time for steam-coal gasification with CaO and alkali hydroxide catalysts, and with no catalyst. We first show experiments conducted using the Wyodak-Anderson sub-bituminous coal at 700 °C, 2.1 MPa. The following experiments for CaO catalyst are presented in Figure 4: (a) coal without catalyst, (b) coal with 8.2 g of CaO mixed dry, and (c) coal with 8.2 g of CaO and 1.0 g of KOH mixed with 30 g of water prior to entering the gasifier. We first discuss the results in Figure 4 showing the flow rate versus time of each of the syngas components. There was an increase in flow rates with the addition of calcium oxide (Figure 4b) compared with no catalyst (Figure 4a), and there was an even larger increase in flow rates with the addition of calcium oxide and potassium hydroxide (Figure 4c) compared with no catalyst (Figure 4a). There is also a noticeable change in the gas composition when adding calcium oxide to the reactor. As expected, the H₂ concentration increases and the CO₂ concentration decreases when adding enough CaO to capture 50% of the carbon in the coal. As seen in Figure 4b&c, the flow rate of carbon dioxide increases with time after there is partial saturation of the calcium oxide; then the flow rate reaches a maximum and decreases along with all of the syngas species as the coal is consumed. In Figure 4a&b, there is a large spike in syngas production near t=0, and this is due to pyrolysis reactions that occur during start-up and early in the gasification phase. This effect is more noticeable in the case without catalyst than in the cases with catalysts because the catalysts increase the steam-coal gasification reaction rates.

Figure 4 also shows the normalized reduction charge remaining in the coal as a function of time. This is a measure of how much chemical oxygen demand is left in the coal, and it goes to zero when all of the carbon and hydrogen in the coal have reacted. In the graphs on the right, it is easy to see the large increase in coal conversation when using CaO and KOH mixed with 30 g of water compared with dry mixing just CaO or using no catalyst with the coal. Another item to highlight in Figure 4 (b) and (c) is that NRCR versus time data shows signs of two separate exponential fits. In other words, there appear to be two distinct reactions occurring with different time scales. The faster kinetics at earlier times is a clear indication that both pyrolysis and steam-coal gasification are occurring at earlier times, whereas at later times, the pyrolysis reactions are complete and only steam-coal gasification reactions are occurring. The evidence for pyrolysis reactions only at the beginning of the experiment includes the observation

that the ethane flow rate decreases much faster than the flow rate of hydrogen. Ethane is a coal pyrolysis product, and is not a steam-coal gasification product.



Figure 4: Left: Flow rate of the syngas components from steam-coal gasification experiments at 700°C and 2.1 MPa using 5 g of Wyodak-Anderson coal and a water flow rate was 0.05 g/min. Right: Normalized reduction charge remaining of the coal versus time for the same experiments. (a) No catalyst, (b) 8.2 g of CaO mixed dry with coal, and (c) 8.2 g of CaO and 1.0 g of KOH mixed with the coal as well as 30 g of water prior to entering the gasifier.

We also present 'vs. time' results for some of the experiments using Pittsburgh#8 coal. Figure 5 shows the flow rates of the major coal gasification product when the reactor pressure and temperature were 2.1 MPa and 800°C and the gasifier was operated either with (a) or without (b) alkali hydroxide catalysts. There was a considerable increase in the reaction rates with catalyst, as seen by the significant increase in the production of hydrogen and methane when catalysts were included with the coal. The production-averaged, dry gas composition in Figure 3 was approximately 80% H₂ and 20% CH₄. This gas composition is only possible if there is significant capture of CO₂ inside the gasifier. In fact, we determined that approximately 80% of the alkali hydroxide species capture CO₂ inside the gasifier and convert into alkali carbonates. To the best of the authors' knowledge, this is the first documented case of using a molten mixture of alkali hydroxides to capture CO₂ inside of a coal gasifier.



Figure 5: Flow rate of the syngas components from experiments at 800°C and 2.1 MPa using 5 g of fresh Pittsburgh#8. Water flow rate was 0.05 g/min. (a) With catalyst [2.7 g LiOH, 4.5 g NaOH, and 6.3 g KOH] and (b) Without catalyst. Note the different x-axis and y-axis scales. Time = 0 is the time at which the reactor reaches 2.1 MPa.

Figure 6 (a) shows the exhaust gas flow rate from gasification of 5 g of Pittsburgh#8 coal (100 mesh), 2.7 g of LiOH, 4.5 g of NaOH, and 6.3 g of KOH at 900°C and 2.1 MPa. At t=0, the gas exits the reactor after reaching a pressure of 2.1 MPa. There was an overall decrease in the total flow rate of syngas with time because the amount of coal in the reactor was slowly consumed. The methane and ethane concentration decreased rapidly for three main reasons: (1) the amount of coal available for reaction decreased with time, (2) pyrolysis reactions occurred mostly at the beginning of the experiment, and (3) the concentration of steam inside of the reactor increased with time because less steam was being

consumed by the coal, and hence the amount of steam available to reform any methane and ethane increased with time. The production of carbon dioxide increased at the beginning of the experiment, and then decreased slowly over the rest of the experiment. This trend is due to a combination of effects: (1) the decreasing amount of coal remaining in the reactor and (2) the decreasing amount of hydroxides to capture CO_2 as the hydroxides convert to carbonates.



Figure 6: (a) Flow rate of the syngas components from a coal-catalyst-steam experiment at 900°C and 2.1 MPa, using 5 g of fresh Pittsburgh#8, 2.7 g of LiOH, 4.5 g of NaOH, and 6.3 g of KOH. Water flow rate was 0.05 g/min. (b) Normalized reduction charge remaining of the coal versus time for the same experiment.

Figure 6 (b) shows the percent remaining of the coal as a function of time for the same conditions as in Figure 6 (a). Note that the data in Figure 6 (b) starts at 90% coal remaining because 10% of the coal is consumed during the pressurization of the reactor. One can see that the fit through the data between 90% and 40% remaining is nearly exponential, i.e. a first-order rate of reaction. For our system, a first-order rate of reaction means either that the rate limiting reaction is only a function of the amount of coal or that the other species in the rate limiting reaction are not varying significantly, such as steam. An exponential fit through the data between NRCR equals 40% and 10% was also nearly exponential, and as expected, the rate constant from 40% to 10% was less than the rate constant between 90% and 40% because the coals studied here contain significant quantities of species that volatilize early in the experiment. It is important to measure the gas composition with these pyrolysis gases (CH₄, C₂H₆, C₂H₄) because there would be significant amounts of pyrolysis gases generated even in a commercial scale catalytic gasifier.

2.3.3 Effect of catalyst type

Table 3 shows the production-averaged, syngas composition from the catalytic gasifier as a function of the type of catalyst for Pittsburgh#8 coal and for Wyodak-Anderson coal, respectively. As described in the experimental set up section, production-averaged means that the total amount of species 'x' produced during the experiment was divided by the total amount of syngas during the experiment. In Table 3, the ratio of alkali-to-carbon was 1:1 and the ratio of alkali earth metal to carbon was 0.5:1. Therefore, there was an equal carbon dioxide capture capability when comparing the alkali hydroxides with the alkali earth catalysts because two moles of alkali hydroxides are required to capture one mole of carbon dioxide, whereas only one mole of alkali earth metal oxide is required to capture one mole of carbon dioxide.

We can see significant capture of both carbon dioxide and hydrogen sulfide when using either alkali hydroxides or calcium oxide by comparing the amount of carbon species in the syngas with the case of no catalyst. There is negligible CO₂ or H₂S capture for the case of calcium silicate. The first-order rate constant was largest for alkali hydroxide catalysts, and this was most evident when using Wyodak-Anderson coal. However, in the case of alkali hydroxide catalysts, the combined hydrocarbon composition of the syngas was lower than when using the other catalysts or no catalyst. This suggests that the alkali catalyst can lower the activation for methane reforming. As mentioned earlier, potassium hydroxide/carbonate has been shown to lower the activation barrier energy of the methanation reaction [15-16], and hence, can lower the activation barrier energy of the reverse reaction, i.e. methane reforming. One possible reason why there was a lower methane composition in the syngas when operating with catalysts compared to when operating without catalysts, as seen in Table 3, is that the catalysts lower the activation energy barrier for the methanation and methane reforming pair of reactions. Since the methane and ethane composition due to coal volatilization is often greater than if the syngas were in chemical equilibrium, the catalysts have the unintended effect of actually decreasing the methane and ethane composition in the syngas. At these temperatures, this can be avoided by operating at higher pressures than studied here.

	H ₂	СН ₄	C ₂ H ₄₋₆	co₂	со	H ₂ S	Rate	Standard Deviation of Rate
Catalyst	%vol	%vol	%vol	%vol	%vol	[ppm]	[hr ⁻¹]	[hr ⁻¹]
Alkali Hydroxide	74	16	2.9	2.9	3.3	13	0.7	+/- 0.2
Lime	51	26	4.8	3.6	15	17	0.4	+/-0.1
Calcium Silicate	45	21	3.4	22	7	5530	0.3	+/- 0.1
No Catalyst	36	27	5.2	17	14	5763	0.2	+/- 0.05

(a) 100 mesh Pittsburgh#8 coal, 2.1 MPa, 700°C.

(b) 100 mesh Wyodak-Anderson coal, 2.1 MPa, 700°C.

	H ₂	CH ₄	C ₂ H ₄₋₆	co₂	со	H ₂ S	Rate	Standard Deviation of Rate
Catalyst	%vol	%vol	%vol	%vol	%vol	[ppm]	[hr ⁻¹]	[hr ⁻¹]
Alkali Hydroxide	73	16	2.3	0.8	7.9	2	1.9	+/- 0.2
Lime	70	18	3.3	0.7	7.9	8	0.7	+/- 0.1
Calcium Silicate	38	15	3.2	24	19	646	0.3	+/- 0.1
No Catalyst	38	20	3.0	28	12	722	0.2	+/- 0.05

2.3.4 Effect of temperature: Coal without catalyst

In the following sections, we convert the data versus time into product-averaged gas composition and a kinetic rate of coal gasification at temperatures between 700°C and 900°C. In Table 4a, we present the experimental gas composition and kinetic rate of coal conversion for Wyodak-Anderson sub-bituminous coal without catalyst as a function of temperature. In Table 4a, we also present the simulated chemical equilibrium gas composition using HSC Chemistry 6 (Outotec Solutions, Espoo, Finland.). To model Wyodak-Anderson coal in HSC Chemistry, we used a mixture of species with the same ratio of C:H:O as given in Table 1. We can model coal this way because, for a given input of ratios of C:H and C:O, the output gas composition from a chemical equilibrium simulation is independent of the molecules used to make up the ratios of C:H and C:O. All of the experiments presented in this section and in the next section were repeated three times at each temperature. The data in the tables are the average composition

to 60% conversion, the kinetic rate to 60% conversion, and the standard deviation of the conversation rate of the three realizations at that temperature. For the Wyodak-Anderson coal, there was an approximately threefold increase in the coal conversion rate between 700°C and 900°C. At 900°C and 2.1 MPa, the conversion rate of the Wyodak-Anderson coal was 0.63 hr⁻¹. For comparison, the conversion rate of the graphite under similar temperature, pressure and steam flow rate was only 0.014 hr⁻¹.

In Table 4b, we present the experimental gas composition and kinetic rate of coal conversion for Pittsburgh#8 bituminous coal without catalyst as a function of temperature. Using HSC Chemistry 6, in Table 4b we also present the calculated gas composition assuming that there is complete chemical equilibrium and 100% coal conversion. To model Pittsburgh coal, we likewise used a mixture of species with the same ratio of C:H:O as given in Table 1. Since HSC Chemistry is a chemical equilibrium calculator, the equilibrium composition is a function of only the temperature, total pressure, and ratio of C:H:O. There was a four-fold increase in the coal conversion rate between the range of 700°C and 900°C. As expected from the chemical equilibrium simulations, at increased temperatures, there was an increase in the carbon monoxide composition and decrease in carbon dioxide composition. As in Table 4a, there was a large difference between the experimental and simulated composition of methane and higher hydrocarbons. A more accurate ability to predict the chemical composition would require knowledge of both the pyrolysis reactions and the rate of breakdown of pyrolysis molecules inside of the gasifier.

As the temperature increased in the chemical equilibrium simulations in Table 4, there was an increase in the carbon monoxide composition, and a decrease in both methane and carbon dioxide composition. However, since a chemical equilibrium simulation cannot account for pyrolysis product gases that are kinetically-limited from reacting before leaving the reactor, there was a large difference between the experimental and simulated composition of methane and higher hydrocarbons. It should be noted that C_2HC in the Tables represents the total ethane and ethylene in syngas. Consistently throughout the experiments, the measured ratio of ethane to ethylene was approximately two; however, we present only the sum of ethane plus ethylene because of the similarity of the two species.

It is also important to note that, given the C:H:O:S ratios in Table 1, the chemical equilibrium dry gas composition of H₂S should be on the order of 1000 ppm for Wyodak-Anderson coal and 2000 ppm for Pittsburgh#8 if all of the organic sulfur in the coal is converted to gaseous products at the same rate as the hydrogen and carbon in the coal. As seen in Table 4, the experimental H₂S gas composition from the

Pittsburgh#8 coal was between approximately 3000 and 6000 ppm and from the Wyodak-Anderson coal was approximately 700 ppm. Therefore, the experimentally measured H₂S gas composition in both the Wyodak-Anderson and Pittsburgh#8 coals were fairly close to the expected values using HSC Chemistry.

Table 4: Product-average gas composition, kinetic rate of coal gasification and standard deviation of kinetic rate to 60% coal conversion for steam-coal gasification at a pressure of 2.1 MPa at temperatures between 700°C and 900°C. Experimental values are shown on the left side of a column and HSC Chemistry 6 numerical chemical equilibrium simulations are shown on the right side of a column in parenthesis.

Temperature	F	\mathbf{I}_2	С	H_4	C ₂	нс	С	O ₂	С	20	H ₂ S	Rate	Standard Deviation of Rate
[°C]	[9	%]	[9	6]	[9	%]	[9	%]	[9	%]	[ppm]	[hr ⁻¹]	[hr ⁻¹]
900	45	(54)	14	(5)	1.5	(0.0)	22	(10)	17	(32)	692	0.63	+/- 0.21
800	47	(53)	16	(8)	2.0	(0.0)	23	(18)	12	(20)	679	0.37	+/- 0.14
700	38	(58)	20	(8)	3.0	(0.0)	28	(27)	12	(8)	722	0.21	+/- 0.05

(a) Wyodak-Anderson sub-bituminous coal without catalyst-capture agent

(b) Pittsburgh#8 bituminous coal without catalyst-capture agent

Temperature	I	\mathbf{H}_2	С	\mathbf{H}_4	C ₂]	нс	С	02	С	0	H ₂ S	Rate	Standard Deviation of Rate
[°C]	[ª	%]	[ª	%]	[]	%]	[9	%]	[ª	%]	[ppm]	[hr ⁻¹]	[hr ⁻¹]
900	36	(45)	21	(11)	3.6	(0.0)	16	(5)	23	(38)	3576	0.82	+/- 0.20
800	32	(47)	28	(14)	4.2	(0.0)	17	(15)	19	(24)	2830	0.51	+/- 0.15
700	36	(57)	27	(9)	5.2	(0.0)	17	(26)	14	(8)	5763	0.19	+/- 0.05

2.3.5 Effect of temperature: Coal with CaO dry mixed

We continue with the analysis of steam-coal gasification experiments as a function of the temperature of the reactor, but now discuss experiments in which calcium oxide is mixed with the coal prior to being added to the reactor. In Table 5a, we present the experimental gas composition and kinetic rate of coal conversion for 5.0 g of Wyodak-Anderson sub-bituminous coal (100 mesh) with 8.2 g of fresh CaO (100 mesh) as a function of temperature. In Table 5a, we also present the simulated gas composition using

HSC Chemistry assuming that there is complete chemical equilibrium. There was a roughly 40% increase in the coal conversion rate between the range of 700°C and 900°C. This increase for the same difference in temperatures was significantly less than without catalyst. As expected from the chemical equilibrium simulations, at increased temperatures, there was an increase in both the carbon monoxide and carbon dioxide composition, and a decrease in hydrogen composition. Since the pyrolysis gas products are kinetically limited from reaching equilibrium, there was a large difference between the experimental and simulated composition of higher hydrocarbons. There was also a large difference between the amount of H_2S that exits the reactor and that calculated assuming chemical equilibrium. As opposed to the case without the addition of CaO, there was more H_2S measured than predicted by chemical equilibrium calculations.

Table 5: Product-average gas composition, kinetic rate of coal gasification and standard deviation of kinetic rate to 60% coal conversion for coal gasification at a pressure of 2.1 MPa at temperatures between 700°C and 900°C. Experimental values are shown on the left side of a column and HSC Chemistry 6 numerical chemical equilibrium simulations are shown on the right side of a column in parenthesis.

Temperature	H	2	Cł	H ₄	C ₂	нс	C	D ₂	С	0	H ₂	S	Coal Conv. Rate	Normalized Capture Percentage
[°C]	[%	6]	[%	6]	[%	[%]		[%]		6]	[p]	om]	[hr ⁻¹]	[-]
900	65	(61)	18	(25)	2.1	(0.0)	5.6	(4.0)	9.5	(10.0)	140	(2)	1.0	65%
800	66	(67)	19	(21)	2.8	(0.0)	3.7	(2.8)	8.4	(8.5)	126	(3)	0.9	70%
700	70	(68)	18	(30)	3.3	(0.0)	0.7	(0.7)	7.9	(1.1)	8	(3)	0.7	79%

(a) Wyodak-Anderson Sub-Bituminous with 8.2 g of CaO (CaO:C of 0.5:1)

(b) Pittsburgh#8-Bituminous with 8.7 g of CaO (CaO:C of 0.5:1)

													Coal	Normalized
Temperature	H	2	Cł	H_4	C ₂	ΗС	C	D ₂	C	0	H ₂	S	Conv.	Capture
					2								Rate	Percentage
[°C]	[%	6]	[%	6]	[%]		[%]		[%]		[pi	om]	[hr ⁻¹]	[-]
900	49	(56)	21	(14)	2.6	(0.0)	7.1	(3.0)	20	(27)	224	(1)	1.3	60%
800	50	(55)	25	(34)	3.6	(0.0)	4.4	(1.8)	17	(10)	97	(2)	0.9	68%
700	51	(64)	26	(35)	4.8	(0.0)	3.6	(1.1)	15	(1)	17	(12)	0.4	74%

In Table 5b, we present the experimental gas composition and kinetic rate of coal conversion for 5.0 g Pittsburgh#8 bituminous coal and 8.7 g of CaO as a function of temperature. Using HSC Chemistry 6, in Table 5b we also present the calculated gas composition assuming that there is complete chemical equilibrium and 100% coal conversion. There was a threefold increase in the coal conversion rate between the range of 700°C and 900°C. This increase for the same range in temperatures was only slightly less than without catalyst. There was less carbon dioxide capture by the calcium oxide addition when operating with Pittsburgh#8 coal than when operating with Wyodak-Anderson coal, but this was to be somewhat expected because of the higher sulfur content and slightly higher ash content of the Pittsburgh#8 coal. As expected from the chemical equilibrium simulations, at increased temperatures, there was an increase in the carbon monoxide and carbon dioxide composition and a decrease in the hydrogen composition. In Table 5a, we also present the percentage of the CaO that converts into CaCO₃. This amount decreases with increased temperatures. Because the Gibbs free energy of forming calcium carbonate increases with increasing temperature, CaO will not be able to capture as much carbon dioxide at higher temperatures. As was the case for the Wyodak-Anderson sub-bituminous coal, there was a large difference between the experimental and simulated composition of methane, higher hydrocarbons and hydrogen sulfide.

2.3.6 Effect of temperature: Coal with molten alkali hydroxides

Table 6 shows the production-averaged, syngas composition from the molten catalytic gasifier as a function of the reactor temperature when the pressure was held at 2.1 MPa and the coal was fresh Pittsburgh#8 and Wyodak-Anderson, respectively. At all temperatures, there was a significant amount of capture of H₂S inside of the gasifier because the production-averaged composition of H₂S without catalyst addition is on the order of 700 ppm for Wyodak-Anderson and on the order of 5000 ppm for Pittsburgh#8 coal. These values without catalysts are significantly greater than the 0-10 ppm and 0-150 ppm, respectively, measured with alkali hydroxide catalysts.

As seen in Table 6a, the highest average methane composition achieved using Pittsburgh#8 coal was 22% while at the same time producing 2.6% ethane + ethylene. Typically, the ratio of ethane to ethylene measured by the mass spectrometer was 2, but we report the sum of these two species because of the significant overlap between these species in the mass spectrometer used in this study. Hence, we use the symbol 'C₂H₄₋₆' to represent the sum of the ethane plus ethylene composition in the syngas. On a

combustion enthalpy basis, the syngas from the Pittsburgh#8 coal at 800°C with 1:1 alkali to carbon ratio was as follows: $H_2 = 43\%$, $CH_4 = 44\%$, $C_2H_{4-6} = 11\%$, CO = 2%. So, while there is a significant amount of hydrogen in the syngas on a molar basis, the hydrogen and methane represent nearly the same combustion enthalpy. The highest average CH₄ composition achieved using Wyodak-Anderson coal was 17% while at the same time producing 1.9% C₂H₄₋₆. On a combustion enthalpy basis, the syngas from the Wyodak-Anderson coal at 800°C with 1:1 alkali to carbon ratio is as follows: $H_2 = 46\%$, $CH_4 = 37\%$, $C_2H_{4-6} = 11\%$, and CO = 6%.

Table 6: Syngas composition and rate of reaction versus temperature to 60% conversion.

Temperature	H_2	CH ₄	C ₂ H ₄₋₆	CO ₂	со	H_2S	Rate	Standard Deviation of Rate
[°C]	[%]	[%]	[%]	[%]	[%]	[ppm]	[1/hr]	[1/hr]
900	65	20	2.6	7.1	5.4	28	1.4	+/- 0.4
800	66	22	2.6	5.0	3.6	148	1.1	+/- 0.4
700	74	16	2.9	2.9	3.3	13	0.7	+/- 0.2
600	82	13	2.8	1.3	1.3	0	0.13	+/- 0.02

(a) Pittsburgh#8, 1:1 alkali to carbon ratio, 2.1 MPa.

(b) Syngas composition and rate of reaction versus temperature to 60% conversion. Wyodak-Anderson coal, 1:1 alkali to carbon ratio, 2.1 MPa

Temperature	\mathbf{H}_2	CH ₄	C ₂ H ₄₋₆	CO ₂	со	H ₂ S	Rate	Standard Deviation of Rate
[°C]	%vol	%vol	%vol	%vol	%vol	[ppm]	[1/hr]	[1/hr]
900	73	17	1.9	2.1	6.8	10	2.4	+/- 0.6
800	70	16	2.3	4.5	7.7	4	2.0	+/- 0.4
700	73	17	2.3	0.5	8.0	2	1.9	+/- 0.2

The amount of CO₂, and to a lesser extent the amount of H₂S and CO, increased with increasing temperatures, whereas the CH₄ and C₂H₄₋₆ composition were a maximum at 800°C for Pittsburgh#8 coal. The maximum of the CH₄ and C₂H₄₋₆ composition at 800°C was due to a combination of effects: temperature, steam composition, and pyrolysis reactions. For example, at higher temperatures, there was

less steam available to reform the methane and ethane into CO and H_2 because of the faster kinetic rates of steam-coal gasification. This, along with increased amount of methane pyrolysis, can offset the decrease in equilibrium methane composition that would be due solely to increased temperatures if the water vapor composition were constant.

While the greatest amount of CH₄ and C₂H₄₋₆ occurred at 800°C for Pittsburgh#8 and 700°C for Wyodak-Anderson, the largest rate of total syngas formation occurred at 900°C for both coal types. We graph the rate constants shown in Table 6a for experiments using fresh Pittsburgh#8 coal at a pressure of 2.1 MPa in Figure 7, which plots the first order rate constant (from NRCR = 90% to NRCR = 40%) versus the inverse of the temperature. For all catalysts, the clear, and expected, trend was that the rate constant increased as the temperature increased. The use of calcium oxide or alkali hydroxide as a catalyst also significantly increased the rate of reaction compared with the cases with no catalyst. For comparison, when steam-gasifying graphite at 900°C and 2.1 MPa, the first order rate constant was only 0.014 hr⁻¹, which is just under two orders of magnitude slower than the rate of steam-gasification of Pittsburgh#8 coal at a similar pressure, temperature and size of particles.

2.3.7 Effect of temperature: Activation energy barrier

By assuming that the gasification reactions follow an Arrhenius rate equation, we estimated an activation energy barrier for the following cases: without catalyst, with lime catalyst having a 0.5:1 Ca:C ratio, and with alkali hydroxide catalyst mixtures having Li:Na:K:C ratios of 1:1:1:3. These values for both Pittsburgh#8 and Wyodak-Anderson coals are summarized in Table 7. The trend of activation barrier energies was expected because (a) a singly charged cation can ion-exchange into more acid groups in coal than a doubly charged cation and (b) the alkali catalyst is in the molten state whereas the alkali earth catalyst remains solid. There is large uncertainty in the calculated values of activation energy barrier because the uncertainty at each temperature propagates into the uncertainty of the energy barrier.

While the general trend from the activation barrier energies makes intuitive sense, it should be noted that these values are the apparent activation barrier energies and should not be interpreted as the intrinsic activation barrier energies for the rate limiting reactions. It would be challenging to obtain one single activation energy barrier in a fuel as complex as coal, and therefore, the values calculated above represent an average activation energy barrier that lumps together the multiple reactions occurring in parallel and in series near the surface of the coal. In addition, the activation barrier energy calculated in the alkali hydroxide case does not include the datum at 600°C, which shows a significant decrease in reaction rate, much larger than implied by the activation barrier energy as suggested for data between 700°C and 900°C. Therefore, the activation barrier energies reported above are not applicable outside of this temperature range, and in addition, these values may be unique to the fixed-bed gasifier design used in these experiments if the chemical reactions were mass transport limited.



Figure 7: Rate constant versus inverse temperature for various catalysts, Pittsburgh#8 coal, 2.1 MPa, to 60% coal conversion. Catalysts were added at an equal capability to capture CO_2 . Ratio of alkali hydroxide to carbon = 1:1, and ratio of CaO to carbon = 0.5:1. Error bars represent the standard deviation of the gasification rate for the three runs at each data point.

Table 7: Effective activation barrier energy in kJ/mol for both coal type and different type of catalyst. The lime case is a ratio of CaO to carbon of 0.5:1, and alkali hydroxide case is a ratio of alkali to carbon of 1:1.

Effective Activation Barrier Energy [kJ/mol]	No Catalyst	Lime	Alkali Hydroxide
Pittsburgh#8	62±13	52±15	37 ±12
Wyodak-Anderson	55±11	15 ± 8	12 ± 6

2.3.8 Effect of catalyst to coal ratio for molten alkali hydroxides

Table 8 and Table 9 show the syngas composition and the reaction rate as a function of the amount of alkali catalyst used. We also include experimental data using potassium carbonate as the catalyst instead of the mixture of alkali hydroxides. Two values of catalyst to carbon ratio were used with potassium carbonate. The 4.6% potassium carbonate is a similar catalyst to carbon ratio as used by Exxon in their catalytic fluidized bed gasifier. The other value was chosen to be similar to 0.25 alkali hydroxide to carbon ratio, so as to highlight the fact that potassium carbonate can be used to capture sulfur species, but it can't be used for in situ capture of carbon dioxide. In the Pittsburgh#8 case, the alkali-to-carbon ratio was varied between 0 and 2, and in the Wyodak-Anderson case, the alkali-to-carbon ratio was varied between 0 and 1. In both cases, there is an increase in carbon dioxide and hydrogen sulfide capture with increasing amounts of alkali hydroxide catalyst. When the alkali-to-carbon ratio was equal to one for both coal types, the alkali hydroxide catalyst captured 99.7% of the sulfur that would have been released if there was no capture agent. Capture of acid gases leads to greater concentration of hydrogen in the syngas because of the increased amount of water vapor available for gasification. There is also a general trend of increasing reaction rate with increasing catalyst amount; however, in the Pittsburgh#8 case, there seems to be a limit to which increasing the catalyst amount can increase the reaction rate. In the Pittsburgh#8 case, there is a trend of decreasing methane and ethane composition with increased catalyst addition, but this trend is largely absent in the Wyodak-Anderson data. This is probably due to the increase in gasification rate, and hence the decrease in the average water vapor composition in the syngas. Too much water vapor in the gasifier will cause reforming of hydrocarbons, which is to be avoided if the goal of the gasifier is to produce a high energy content syngas. From the

data in these tables, it appears that potassium carbonate and alkali hydroxide mixtures are equally effective at catalyzing the steam-coal gasification reaction, as well as capturing hydrogen sulfide. The main difference is the capability for hydroxides to capture CO_2 in the gasifier. In section 2.4.2, we will compare the experimental data and the chemical equilibrium simulations in Table 8.

 Table 8: Syngas composition and rate of reaction versus catalyst amount. Pittsburgh#8 coal to
 60% conversion, 2.1 MPa, 700°C.

Ratio of Alkali Metal in Catalyst to Carbon in Coal	H2 [%]	CH ₄ [%]	C ₂ H ₄₋₆ [%]	CO ₂ [%]	CO [%]	H ₂ S [ppm]	Rate [1/hr]	Standard Deviation of Rate [1/hr]
2.0 (Eutectic Hydroxide)	78	14	2.2	1.0	4.3	8	0.6	+/- 0.2
1.0 (Eutectic Hydroxide)	73	16	2.8	4.0	3.5	13	0.6	+/- 0.2
0.5 (Eutectic Hydroxide)	63	20	3.5	6.3	6.5	119	0.6	+/- 0.2
0.25 (Eutectic Hydroxide)	61	23	3.4	10	2.7	106	0.6	+/- 0.2
0.28 (Potassium Carbonate)	36	22	3.5	21	18	35	0.68	+/- 0.06
0.125 (Eutectic Hydroxide)	42	22	3.7	17	15	108	0.54	+/- 0.10
0.046 (Potassium Carbonate)	41	19	2.8	26	12	689	0.32	+/- 0.04
0.0 (No Catalyst)	36	27	5.1	17	15	5625	0.19	+/- 0.05

(a) Experimental Data

(b) Chemical Equilibrium Simulations

Ratio of Alkali Metal in Catalyst to Carbon in Coal	H ₂ [%]	CH ₄ [%]	C ₂ H ₄₋₆ [%]	CO ₂ [%]	CO [%]
2.0 (Eutectic Hydroxide)	99.9	0.06	0.0000	0.01	0.01
1.0 (Eutectic Hydroxide)	97	2	0.0000	1	0
0.5 (Eutectic Hydroxide)	72	13	0.0004	10	4
0.25 (Eutectic Hydroxide)	61	13	0.0004	18	7
0.28 (Potassium Carbonate)	51	13	0.0006	26	9
0.125 (Eutectic Hydroxide)	59	11	0.0003	22	7
0.046 (Potassium Carbonate)	60	7	0.0001	26	7
0.0 (No Catalyst)	59	7	0.0001	26	7

 Table 9: Syngas composition and rate of reaction versus catalyst amount. Wyodak-Anderson coal

 to 60% conversion, 700°C, 2.1 MPa.

(a) Experimental Data

Ratio of Alkali Metal in Catalyst to Carbon in Coal	H ₂ [%]	CH4 [%]	C ₂ H ₄₋₆ [%]	CO ₂ [%]	CO [%]	H ₂ S [ppm]	Rate [hr ⁻¹]	Standard Deviation of Rate [hr ⁻¹]
1.0 (Eutectic Hydroxide)	73	16	2.3	0.8	7.9	2	1.9	+/- 0.2
0.5 (Eutectic Hydroxide)	69	14	2.2	8.2	7.3	2	1.6	+/- 0.3
0.25 (Eutectic Hydroxide)	55	11	2.3	23	9.3	148	0.35	+/- 0.05
0.28 (Potassium Carbonate)	47	13	1.6	30	9.0	112	0.34	+/- 0.05
0.0 (No Catalyst)	38	20	3.0	28	12	722	0.21	+/- 0.05

(b) Chemical Equilibrium Simulations

Ratio of Alkali Metal in	H_2	CH ₄	C ₂ H ₄₋₆	CO ₂	СО
Catalyst to Carbon in Coal	[%]	[%]	[%]	[%]	[%]
1.0 (Eutectic Hydroxide)	79	20	0.0008	0.5	0.8
0.5 (Eutectic Hydroxide)	75	18	0.0007	4.1	2.7
0.25 (Eutectic Hydroxide)	64	9.3	0.0002	20	6.5
0.28 (Potassium Carbonate)	55	10	0.0003	27	8.4
0.0 (No Catalyst)	62	4.6	0.0001	27	6.5

2.3.9 Effect of steam to coal ratio for molten alkali hydroxides

Table 10 shows the syngas composition and the first-order reaction rate constant as a function of the ratio of steam to carbon in the coal. The water flow rate is given in units of the mol·hr⁻¹ of water vapor entering the reactor normalized by the original moles of carbon in the coal. The clear trend was an increase in the amount of hydrogen and a decrease in the amount of methane in the syngas with an increase in the rate of water injection to the gasifier. In this case, the water vapor was reforming methane and ethane into hydrogen within the gasifier, but this did not cause an increase in the total amount of CO and CO₂, implying there was an increase in the amount of CO₂ capture with increased levels of water vapor. Quite interestingly, the first-order rate constant [hr⁻¹] was often larger than the normalized water flow rate [hr⁻¹]. This is partially due to the fact that volatilization reactions do not require water vapor, but it also implies that the water required for steam-coal gasification reaction is being supplied by the hydroxide species in the alkali hydroxide. For example, in the case of zero water addition, there is significant coal consumption without any water addition, other than water that evolves from an alkali hydroxide species when alkali hydroxide species either (a) capture acid gases, (b) cation exchange with

a proton on an acid group in the coal, or (c) convert into an alkali oxide (such as Na_2O). Within the standard deviation in the data, the results in Table 10 suggest that the amount of water vapor does not have a strong effect on the rate of reaction, though it should be noted that water vapor would be required to achieve 100% conversion of the coal.

Table 10: Syngas composition and rate of reaction versus water flow rate. Pittsburgh#8 coal to 60% conversion, 700°C, 1:1 alkali to carbon ratio. Water flow rate is given in units of mol $H_2O \cdot (mol C)^{-1}$ $\cdot hr^{-1}$ of water vapor entering the reactor normalized by the original carbon in the coal. The standard value used for water flow rate in other experiments was 0.56 mol $H_2O \cdot (mol C)^{-1} \cdot hr^{-1}$.

Water Flow Rate	H ₂	CH ₄	C ₂ H ₄₋₆	CO ₂	СО	H_2S	Rate	Standard Deviation of Rate
$[\text{mol H2O} \bullet (\text{mol C})^{-1} \bullet \text{hr}^{-1}]$	%vol	%vol	%vol	%vol	%vol	[ppm]	$[hr^{-1}]$	$[hr^{-1}]$
1.12	79	14	2.2	3.1	1.5	11	0.4	+/- 0.1
0.56	74	16	2.9	2.9	3.3	13	0.7	+/- 0.2
0.28	69	19	4.0	3.5	4.0	20	0.4	+/- 0.1
0.0	65	25	3.5	1.5	5.2	11	0.6	+/- 0.2

2.3.10 Effect of pressure for molten alkali hydroxides

In this set of experiments, both Pittsburgh#8 and Wyodak-Anderson coals were de-volatilized before use in the reactor because we wanted to rule out any change in the amount of volatile gases as a function of pressure. At 700°C and at 2.1 MPa, both coals released 30% of their chemical oxygen demand after de-volatilization for five hours. On a molar basis, the pyrolysis gas composition was 41% CH₄, 7% H₂, 5% CO₂, 36% CO, 9% C₂H₄₋₆ and 2% H₂S for the Pittsburgh#8 coal and was 26% CH₄, 23% H₂, 23% CO₂, 22% CO, 6% C₂H₄₋₆ and 0.4% H₂S for the Wyodak-Anderson coal. As far as the original chemical oxygen demand of the coal, this represents: 18% CH₄, 0.8% H₂, 4.0% CO, and 7.0% C₂H₄₋₆ for Pittsburgh#8 and 12% CH₄, 2.6% H₂, 2.4% CO, and 4.7% C₂H₄₋₆ for Wyodak-Anderson.

Table 11 shows the syngas composition, as well as the kinetic rates of steam-coal gasification, as a function of pressure of the vessel, when the temperature was held constant at 700°C. As expected, there was an increase in the methane concentration as the pressure was increased. In addition, increased pressure also increased the reaction rate constants.

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Pressure	H_2	CH₄	$C_{2}H_{4,6}$	CO ₂	CO	H ₂ S	Rate	Standard
[MPa]	Г0/,1	Г0/, 1	- <u>2</u> 4-0	Г0/1	[%]	[nnm]	$[hr^{-1}]$	Deviation of
	[\0]	[/0]	[/0]	[/0]	[,0]	[hhu]		Rate [hr ⁻¹]
0.1	80	1.8	1.2	11	5.6	23	0.42	+/- 0.10
0.4	81	2.9	1.6	13	2.4	N/A	0.39	+/- 0.04
1.0	87	8.1	2.4	1.5	2.0	4	0.59	+/- 0.28
2.1	80	13	2.6	3.5	2.3	4	0.64	+/- 0.08

Table 11: Syngas composition and rate of reaction versus pressure. Pre-devolatized Pittsburgh#8coal to 60% conversion, 700°C, 1:1 alkali to carbon ratio.

2.3.11 Cycle degradation using CaO only

Here, we discuss results of repeated CaO-CaCO₃ cycles. Before discussing experimental results from repeated CaO-CaCO₃ cycles, it is important to highlight why the following data sets were collected using only Wyodak-Anderson coal. For multiple cycles of gasification with CO₂ capture and regeneration of CaO, it is likely that Wyodak-Anderson coal would make a better choice than Pittsburgh#8 coal. The reasons are the following: (1) the kinetic rate of steam-coal gasification was slightly higher at 700° C; (2) the normalized capture percentage was slightly higher; and most importantly (3) there is less sulfur and silica-aluminates in the coal, which, as we will discuss in section 2.4.2, has a large impact on the amount of make-up CaCO₃ required to meet requirements to sell the purge-stream to a cement kiln. For these reasons, we chose to use only the Wyodak-Anderson coal in the CaO-CaCO₃ cycle degradation discussed in the next two sections.

We present results on the degradation of the regenerated calcium oxide to capture carbon dioxide and hydrogen sulfide. In Table 12, we present the following: (1) the syngas composition during gasification, (2) the first-order coal conversion rate to 40% reduction charge remaining, (3) the percentage of the calcium oxide that captures CO_2 , and (4) the first-order release rate of the calcium carbonate during regeneration/calcination. The results in Table 12 represent an average of two experiments, where each experiment was conducted out to six cycles of gasification/carbonation and regeneration/calcination. For example, the material mixed with the 5.0 g of fresh coal in Cycle#2 was the material recovered from the regeneration (calcination) phase of Cycle#1. The amount of material recovered from after each cycle increased from ~8 g to ~10 g between Cycle#1 and Cycle#6 because of the ash in the coal. The weight recovered was consistent with the material being mostly CaO rather than Ca(OH)₂.

Table 12: Results versus cycle number for 5.0 g of Wyodak-Anderson coal and initially 8.2 g of CaO. Gasification occurred at 2.1 MPa, 700 °C. CaO regeneration occurred at 0.1 MPa, 900°C, and the CaO was then reused in the next cycle with fresh coal. Results include: syngas composition during gasification, the first-order coal conversion rate out to 40% reduction charge remaining, the percentage of the calcium oxide that captures CO₂, and the first-order release rate of the calcium carbonate during regeneration (calcination).

								Normalized	CO ₂
							Coal Conv.	Capture	Release
	H ₂	CH_4	C_2HC	CO ₂	CO	H ₂ S	Rate	Percentage	Rate
	[%]	[%]	[%]	[%]	[%]	[ppm]	[hr ⁻¹]	[-]	[hr ⁻¹]
Cycle#1	82	10	1.3	3.0	3	6	0.7	79%	2.7
Cycle#2	80	11	1.4	3.4	5	16	0.7	78%	3.6
Cycle#3	80	11	1.7	3.6	4	8	0.7	70%	3.3
Cycle#4	81	11	1.3	3.7	3	25	0.6	74%	2.5
Cycle#5	81	10	1.2	4.7	3	42	0.7	73%	3.1
Cycle#6	76	11	1.3	7.4	4	40	0.6	67%	3.2

There are a few important trends with increasing cycle number: (a) the coal gasification rate does not significantly change; (b) the capture percentage decreases roughly 2-3% after each cycle; (c) there is a slight increase in the sulfur composition; and (d) there is not a significant change in the CO₂ release kinetic rate. Because there is less CO_2 capture by the calcium oxide with increasing cycle number, this shows up in the syngas composition as higher values of carbon dioxide and lower values of hydrogen, but there is no significant change in methane, ethane or carbon monoxide composition. It should also be noted that the average degradation rate per cycle that we measured was consistent with the results from prior studies (as summarized in Weimer *et al.* [36]). The silica-aluminates and the sulfur in the ash can react with CaO to form species that cannot capture carbon dioxide, as will be discussed further in section 2.4. If these reactions are not kinetically limited, the ash in the coal could account for a degradation of roughly 3% per cycle and the sulfur in the coal could account for a degradation of roughly 1% per cycle, for a combined degradation of roughly 4% per cycle. Therefore, we conclude that the cause of the degradation in the capture ability is likely the sulfur and the silica-aluminates in the ash.

In Table 13, we present a single cycle experiment in which fresh lime and the Wyodak-Anderson coal were mixed with 30 g of water prior to coal gasification. This single cycle test was repeated 3 times, and the average values from the three runs are shown in Table 13. One noticeable effect was that the amount

of hydrocarbons in the syngas increased significantly compared with an exactly similar experiment, but without aqueous mixing of the coal and CaO. There was also a slight increase in the gasification kinetics when the CaO was mixed aqueously with the coal compared with the results in Table 12 without H_2O addition prior to gasification. While the addition of water increased the kinetic rate, we discuss in the next section a means to further increase the steam-coal gasification kinetics.

Table 13: Results 5.0 g of Wyodak-Anderson coal, 8.2 g of CaO, and 30 g of H₂O. Gasification occurred at 2.1 MPa, 700 °C, and CaO regeneration occurred at 0.1 MPa, 900 °C.

								Normalized	CO ₂	
							Coal Conv.	Capture	Release	Carbon
	H ₂	CH_4	C_2HC	CO_2	СО	H ₂ S	Rate	Percentage	Rate	Balance
	[%]	[%]	[%]	[%]	[%]	[ppm]	[hr ⁻¹]	[-]	[hr⁻¹]	[%]
Cycle#1	72	18	4.7	0.2	5.0	1	1.1	78%	2.2	95

2.3.12 Cycle degradation using both CaO and KOH

In this set of experiments, we studied the effect of adding small amount of potassium hydroxide to the coal and calcium oxide in order to increase the rate of reaction. We conducted these experiments because the steam-coal gasification kinetic rates using only CaO, as was seen in Table 12 and Table 13, were only on the order of 1 h⁻¹. This is not particularly fast compared with gasification rates in oxygenblown gasifiers $\sim 1 \text{ s}^{-1}$ [72]. Therefore, in order to increase the kinetic rate, and hence decrease the reactor size for a given required flow rate of syngas, we evaluated the impact of adding 1 g of KOH to the 8.2 g of CaO added at the start of a set of six cycles. In addition, to further to improve the capability of KOH to catalyze reactions with coal, we have mixed the CaO and KOH with the coal and 30 g of water. Mixing alkali or alkali earth catalyst with coal and water has been shown by previous authors [73-76] to increase the ability of the alkali to catalyze steam-coal gasification because the alkali and alkali earth species can ion exchange with protons from carboxylic acid and hydroxyl groups in the coal. In particular, the CaO plays in important role inside the gasifier in keeping the potassium in an active form so that the alkali species is free to catalyze reactions with the coal [77]. In section 2.4, we will discuss further how CaO keeps potassium in an active form. It should also be noted that it is possible for the KOH to affect the capture ability of the CaO and the temperature required for desorption [78].

In the experiments presented in this section, the gasification and regeneration steps were conducted exactly the same as the last section, except that 1.0 g of KOH was added before the first cycle and that

Table 14 shows results, similar to Table 12, in which a series of six CaO gasification / CaCO₃ calcination cycles were performed to measure the degradation in the ability of regenerated catalysts and capture agents to catalyze steam-coal gasification and to capture carbon dioxide and hydrogen sulfide. In Table 14, we present the syngas composition during gasification, the first-order coal conversion rate out to 40% reduction charge remaining, the percentage of the calcium oxide that captures CO₂, and the first-order release rate of the calcium carbonate during regeneration (calcination). As in Table 12, each data point represents an average of two experiments, where each experiment was taken out to six cycles. With increasing cycle number, the overall trends in these results were the following: (a) decreasing hydrogen and increasing carbon dioxide and carbon monoxide; (b) no significant decrease in the ability to capture H₂S; (c) no significant change in the kinetic rate; and (d) slight decrease in the CO₂ release rate during the regeneration phase. As in the pure CaO-CaCO₃ case, the CO₂ capture percentage decreased roughly 2-3% after each cycle.

Compared with the results in Table 12, there were clear advantages of adding 1 g of KOH with the calcium oxide before the first experiment and mixing the regenerated catalyst aqueous with the fresh coal before each experiment. There was a roughly threefold increase in the coal gasification conversion rate with than when only the regenerated calcium oxide is dry mixed with the coal. The 1.0 g of alkali hydroxide represents a K:C molar ratio of 0.06. This value of $\sim 2.2 \text{ hr}^{-1}$ is close to the value of 1.9 hr^{-1} we measured in previous work [79] using the same pressure, coal-type, temperature and steam flow rate, but using a 1:1 molar ratio of alkali hydroxide to carbon when the Wyodak-Anderson coal and catalyst were dry mixed before loading into the reactor. This value of $\sim 2.2 \text{ hr}^{-1}$ is well above the value of 0.34 hr^{-1} we measured in previous work [79] under the same conditions, but with the dry mixing of a $\sim 0.25:1$ molar ratio of alkali to carbon (when the alkali was either in the form of alkali carbonate or alkali hydroxide.) This value of $\sim 2.2 \text{ hr}^{-1}$ we herefore conclude that the reason for the significantly improved kinetics was a combination of using an alkali hydroxide and aqueously mixing the catalyst with the coal. Using only 1 g of potassium carbonate or only aqueously mixing CaO with the coal and water.

Table 14: Cycle results with 5.0 g of Wyodak-Anderson coal and initially 8.2 g of CaO and 1 KOH. Gasification occurred at 2.1 MPa, 700 °C. CaO regeneration occurred at 0.1 MPa, 900°C, and the CaO was then reused in the next cycle with fresh coal. Results include: syngas composition during gasification, the first-order coal conversion rate out to 40% reduction charge remaining, normalized capture percentage during gasification, CO₂ release rate during calcination, and overall carbon exiting reactor during gasification and calcination normalized by carbon in the input coal.

								Normalized	CO ₂
								Capture	Release
	H ₂	CH_4	C ₂ HC	CO ₂	CO	H ₂ S	Rate	Percentage	Rate
	[%]	[%]	[%]	[%]	[%]	[ppm]	[hr ⁻¹]	[-]	[hr ⁻¹]
Cycle#1	73	16	3.9	0.2	7.0	21	2.3	79%	3.0
Cycle#2	74	16	3.1	0.7	6.8	2	1.9	75%	3.2
Cycle#3	75	13	3.0	0.8	7.8	5	2.0	74%	3.5
Cycle#4	77	13	2.9	0.8	5.4	28	2.6	74%	2.4
Cycle#5	69	17	3.7	1.8	8.2	9	2.2	70%	2.4
Cycle#6	67	14	2.7	5.6	11	2	2.1	60%	2.7

2.4 Discussion & Analysis

2.4.1 Comparison with chemical equilibrium simulations

In this section, we compare the experimental results using alkali hydroxides with thermodynamic simulations using HSC Chemistry (Outotec Solutions, Espoo, Finland), which calculates the chemical equilibrium gas composition as a function of temperature, pressure, and inlet species. By comparing the experimental results with simulation, we were able to make some general conclusions about the degree to which the output syngas was in chemical equilibrium. In HSC Chemistry, we modelled Wyodak-Anderson ($CH_{0.86}O_{0.18}$) and Pittsburgh#8 ($CH_{0.8}O_{0.08}$) using combinations of anthracene ($C_{14}H_{10}$), benzyl benzoate ($C_{14}H_{12}O_{2.0}$), and water (H_2O) in order to obtain the same ratio of C:H:O as the coal, as given in Table 1. We did not include sulfur or nitrogen in the coal in these HSC Chemistry simulations; however, for some simulations listed below we included the alumina-silicates in the coal in order to

estimate the amount of catalyst deactivated by the ash in the coal. When nitrogen and sulfur can be ignored, the equilibrium composition of gases in a hypothetical molten catalytic gasifier is only a function of pressure, temperature, H/C, O/C, and X/C (where H, C, O, and X are the amounts of hydrogen, carbon, oxygen and alkali elements entering the gasifier, respectively.)

Using the data from Figure 6 (900°C, 2.1 MPa), the average composition to 99% conversion was 63% H_2 , 14% CH_4 , 3% C_2H_{4-6} , 10% CO, and 10% CO₂ on a dry molar basis. However, the predicted equilibrium gas composition using HSC Chemistry was 74% H_2 , 4% CH_4 , 0% C_2H_{4-6} , 16% CO and 5% CO₂ on a dry molar basis. As expected, a chemical equilibrium solver will drastically underestimate the composition of C_2 + hydrocarbons in the syngas because volatilization is a reaction that occurs far-from chemical equilibrium. These hydrocarbon de-volalitization reactions are highly dependent on the surface properties of the coal [80]. In the experimental reactor, many of the C_2 + hydrocarbons that volatilize from the coal exit the reactor before they can chemically react, even when there is a significant amount of alkali catalyst. The methane and ethane reforming reactions appear to be kinetically limited, even though there are significant quantities of alkali hydroxides in the reactor. Similar results have been found in fixed-bed reactors, in which two-bed, partial-equilibrium models often have to be created in order to model the gas composition leaving the reactor [81].

In addition, it appears that the CO_2 capture reactions are kinetically limited. For example, from the experimental results in Figure 4, there was a total of 0.19 mol of C that exited the reactor either as CO_2 , CO, CH_4 or C_2H_{4-6} . So, of the original 0.31 mol of C in the coal, 0.12 mol of C was captured by the molten alkali hydroxides. Since there was 0.31 mol of alkali hydroxides added to the reactor, there could have been 0.155 mol of C captured. This means that there is incomplete capture of CO_2 by the alkali hydroxides. We calculated a capture efficiency using the following equation:

$$Capture \ Efficiency = \frac{Carbon \ in \ Orginal \ Coal \ [mol] - Carbon \ in \ Syngas \ [mol]}{\frac{1}{2} \cdot Alkali \ Hydroxide \ [mol] + Calcium \ Oxide \ [mol]}}$$
(7)

Using the data from Figure 4 (900°C, 2.1 MPa), we measure a capture efficiency of 80%. This should be compared with estimates from HSC Chemistry, which predict roughly 90% capture efficiency. The reason that HSC Chemistry predicts only 90% capture efficiency is that (a) ash and sulfur in the coal will react with the alkali hydroxides, and (b) there will still be small amounts of alkali hydroxides in chemical equilibrium. Therefore, the fact that the experimental capture efficiency is less than the capture efficiency predicted by chemical equilibrium suggests that the capture reaction is kinetically limited.

We now discuss HSC Chemistry results as a function of the catalyst to carbon ratio so that we can compare with the experimental results as a function of the catalyst to carbon ratio. Table 8 (b) and Table 9 (b) list the simulated equilibrium gas compositions using same amount of coal, alkali hydroxide and water vapor is in the experiments in Table 8 (a) and Table 9 (a). As expected, there are significant differences between the experimental results and the chemical equilibrium simulations. We conclude: (1) The methane and ethane compositions were much higher than would be expected if the gasifier were at chemical equilibrium. This means that most of the methane and ethane products were volatilization products of the coal that did not react before leaving the reactor. (2) There was less CO_2 capture measured experimentally than would be expected if the gasifier were at chemical equilibrium. This suggests that the CO_2 capture reaction was kinetically limited.

Now, we discuss the functional form of efficiency of capturing carbon inside of the gasifier as a function of the amount of CaO added to the gasifier. We do so at a temperature of 700°C and a pressure of 2.1 MPa, as in gasification/carbonator portion of the CaO-CaCO₃ cycle presented earlier. Using HSC Chemistry, we calculated the syngas composition as a function of the amount of CaO/C added to the gasifier. Using Equation (10) above, we were able to calculate the capture efficiency as a function of the amount of capture agents. In Figure 8, we plot the capture efficiency of the capture agents as a function of the ratio of the input capture agent to input carbon. In Figure 8, we plot the results both including and ignoring the ash and sulfur in the coal. The ash and sulfur only significantly affect the capture efficiency at low values of the input CaO/C. One can see that the capture efficiency should stay above 90% while CaO/C is above 0.6. One reason that the capture efficiency does not stay near 90% until 1.0 and then drop significantly is that CaO+CH₄ is thermodynamically favored over CaCO₃ at this pressure and temperature, even with significant amounts of CaO. This can be seen in Figure 9, which shows the kmol of syngas and the kmol of solids materials as a function of the amount of CaO added to the gasifier. The chemical equilibrium values were calculated using HSC Chemistry, given an input of $C_{14}H_{10}(s) + 20$ $H_2O(g) + x CaO$ at a temperature of 700°C and a pressure of 2.1 MPa, where x is the amount of kmol of CaO, which is shown on the x-axis normalized by the carbon in the fuel. Due to the inability to significantly capture methane, there are limits to the amount of carbon that can be captured in the gasifier. While CaO can be used to capture the CO and CO₂ that would be in the gasifier, there are diminishing returns for increasing the amount of CaO to the gasifier once all of the CO and CO₂ have been captured. This is the main reason that we added CaO at a ratio of 0.5 with respect to the amount of carbon. Larger amounts would not have had a significant effect on the syngas composition exiting the reactor.



Figure 8: Capture efficiency as a function of the ratio of the input CaO to input carbon. Chemical equilibrium simulation using HSC Chemistry



Figure 9: Syngas and Solids amounts as a function of the amount of CaO added to the gasifier. Chemical equilibrium simulation using HSC Chemistry. Input = C14H10(s) + 20 H2O(g) + CaO. T = 700°C and p = 2.1 MPa.
2.4.2 Coal gasification without steam addition

It is important to emphasize the interesting result in Table 10 of coal conversion without any water, just alkali hydroxides. This experiment, like all other experiments, was repeated 3 times, and in each case, there was greater than 60% coal conversion, i.e. less than 40% reduction charge remaining. In fact, the rate of syngas production was three times larger than the production of syngas from the Pittsburgh#8 coal without catalyst but with steam. As discussed in section 3.6, only 30% of the chemical oxygen demand was released during pyrolysis of coal in the absence of alkali hydroxides. To achieve 60% conversion of the coal and to have the gas composition listed in Table 10, the material inside of reactor after the experiment would contain 40% of the chemical oxygen demand of the original coal, contain virtually no hydrogen, and have an alkali:carbon:oxygen ratio of 1.0:0.7:1.0. This ratio of alkali:carbon:oxygen implies that the material remaining in the reactor is not solely composed of some combination of unconverted carbon and alkali carbonates. The material is deficient in oxygen listed above could be formed from a combination of carbon, alkali carbonate, and alkali oxide.

Using the 'with steam' results from Figure 6 out to $\sim 100\%$ conversion and assuming water gas shift equilibrium, we were able to determine that the material remaining in the reactor had virtually no hydrogen had an alkali:carbon:oxygen ratio of 1.8 : 1.0 : 3.0, which is similar to the elemental ratio of alkali carbonate to within the uncertainty in the measurements. As expected, if there is sufficient water vapor in the reactor, the material remaining in the reactor will be alkali carbonates. If there is insufficient water vapor, the 'no steam' results in Table 10 suggest that the material remaining in the reactor will be a combination of unconverted carbon, alkali carbonate and alkali oxide.

Alkali carbonates and hydroxides are more stable than alkali oxides at these temperatures, given that the change in Gibbs free energy is positive for each of the individual alkali hydroxide decomposition reactions.

$$2 \operatorname{LiOH}(s) + C(s) \leftrightarrow \operatorname{Li}_2O(s) + CO(g) + H_2O(g) \qquad \Delta H^{1000K} = + 200 \text{ kJ/mol} \qquad \Delta G^{1000K} = + 7 \text{ kJ/mol}$$

$$2 \operatorname{NaOH}(s) + C(s) \leftrightarrow \operatorname{Na}_2O(s) + CO(g) + H_2O(g) \qquad \Delta H^{1000K} = + 269 \text{ kJ/mol} \qquad \Delta G^{1000K} = + 102 \text{ kJ/mol}$$

$$2 \operatorname{KOH}(s) + C(s) \leftrightarrow \operatorname{K}_2O(s) + CO(g) + H_2O(g) \qquad \Delta H^{1000K} = + 334 \text{ kJ/mol} \qquad \Delta G^{1000K} = + 149 \text{ kJ/mol}$$

The large positive values of the alkali hydroxide decomposition reactions suggest that the alkali

hydroxides will not convert to bulk alkali oxides species. Though, it is possible that alkali oxides species could form on surface of the coal surface or in the molten bed of alkali hydroxides and carbonates. We were unable to model interactions of alkali oxides with surfaces or in the molten mixtures using HSC Chemistry.

Prior research into catalytic gasification by Wood *et al.[82]* and Wigmans *et al.*[83] concluded that carbon will develop a surface with a sub-stoichiometric amount of oxides and with an excess of the alkali metal. Mims and Pabst[44] concluded that the active catalyst sites are complexes similar to alkali phenolate. The 'no steam' results in Table 10 suggest that gasification of coal can proceed in the absence of water vapor or carbon dioxide because alkali hydroxides can convert to alkali oxide species either on the surface of the remaining coal or in the molten bed.

2.4.3 Cold gas efficiency of molten catalytic gasifier

(8)

We first address the general question: what is the efficiency in converting the coal into syngas using a molten hydroxide catalytic gasifier? Since the flow rate data presented in Figure 6 (900°C, 2.1 MPa, 1:1 alkali-to-carbon) was collected up to \sim 1% coal reduction charge remaining (NRCR), we calculated the cold-gas efficiency of this reactor at this temperature and pressure to be 115%. This means that the chemical enthalpy of the syngas leaving the molten hydroxide gasifier is greater than the chemical enthalpy in the original coal, even though the total reduction charge of the syngas was nearly exactly equal to the original reduction charge of the coal. The equation used to calculate the cold gas efficiency is the following:

$$CGE = \frac{\int_0^\infty (242 \, \dot{n}_{H_2} + 283 \, \dot{n}_{CO} + 803 \, \dot{n}_{CH_4} + 1428 \, \dot{n}_{C_2H_6}) dt}{m_{coal} \cdot h_{coal}}$$

Where CGE is the cold gas efficiency, m_{coal} is equal to the mass of the coal added to the reactor in [g], h_{coal} is equal to the higher heating value of coal in [kJ/g] at standard conditions, and where \dot{n}_i is the flow rate in [mol/s] of the syngas species that can be oxidized. The reason that the cold-gas efficiency is greater than 100% is that steam-coal gasification reactions are endothermic. Some of thermal energy required to offset this endothermic reaction is supplied by the exothermic CO₂ capture reaction inside of

the gasifier. For example, at 1000 K, the CO₂ capture by sodium hydroxide releases -174 kJ/ mol CO₂:

$$CO_2(g) + 2KOH(l) \leftrightarrow K_2CO_3(l) + H_2O(g) \quad \Delta H^{1000K} = -179 \text{ kJ / mol}$$
(9)

If one divides the total chemical combustion enthalpy in the exit syngas by the combustion enthalpy in the coal plus the enthalpy of CO_2 capture, one obtains a modified cold gas efficiency (MCGE) of 97%, i.e. 97% of the chemical enthalpy in the coal and hydroxides is converted into chemical reaction enthalpy of the exiting syngas. The equation used for the MCGE is the following:

$$MCGE = \frac{\int_{0}^{\infty} (242 \, \dot{n}_{H_2} + 283 \, \dot{n}_{CO} + 803 \, \dot{n}_{CH_4} + 1428 \, \dot{n}_{C_2H_6}) dt}{m_{coal} \cdot h_{coal} + m_{capture} \cdot h_{capture}}$$
(10)

Where $m_{capture}$ is equal to the mass of the capture agents added to the reactor in [g], and $h_{capture}$ is equal to the enthalpy released in CO₂ capture [kJ/g]. Since the MCGE in this case is nearly 100%, this means that the gasifier could be operated without oxygen and without heat addition, as long as heat transfer from the gasifier to the surroundings can be minimized.

2.4.4 CO₂ capture and CaO degradation mechanisms

In general, there are two main factors that limit the number of times that capture materials could be re-used in the CaO-CaCO₃ cycle: (1) degradation in the capture capability after repeated cycles; and (2) for the particular case of selling the bleed-stream, limits in the CaSO₄ and ash content specified by the cement kiln. Here we discuss degradation in the capture capability due to interaction with species in the coal ash. In the next section, we discuss limitation due to ash & sulfur limits set by a cement kiln. One goal of these two sections is to explain the rationale behind collecting data out to only 6 six cycles in previously discussed research on the CaO-CaCO₃ cycle.

As was seen in Table 12 and Table 14, the capability to capture carbon dioxide decreases with increasing cycle number. To some extent, the capability to capture hydrogen sulfide decreases as well. In Table 15, we present a list of the chemical enthalpy and Gibbs free energy for important gas/solid

phase reactions in the coal gasifier. To minimize space, we have not shown chemical reactions that are combinations of the ones below. Note that the values of ΔH and ΔG are given at 1000 K and for all gases at partial pressures of 0.1 MPa. The reaction enthalpies and Gibbs free energies of the reactions were calculated using HSC Chemistry 6.

Reaction	ΔH^{1000K}	ΔG^{1000K}
	$[kJ \cdot mol^1]$	$[kJ \cdot mof^1]$
$CO_2(g) + CaO(s) \rightarrow CaCO_3(s)$	-169	-23
$CaCO_3(s) + SiO_2(s) \rightarrow CO_2(g) + CaSiO_3(s)$	+79	-68
$CaCO_3(s) + Al_2SiO_5(s) \rightarrow CaAl_2SiO_6(s) + CO_2(g)$	+101	-60
$CaO(s) + H_2S(g) \rightarrow CaS(s) + H_2O(g)$	-60	-61
$CaO(s) + FeS(s) \rightarrow CaS(s) + FeO(s)$	-11	-11
$CaSiO_3(s) + H_2S(g) \rightarrow CaS(s) + SiO_2(s) + H_2O(g)$	+30	+30
$CaAl_2SiO_6(s) + H_2S(g) \rightarrow CaS(s) + Al_2SiO_5(s) + H_2O(g)$	+8	+21
$CaSiO_3(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g) + SiO_2(s)$	-122	-15
$2 \text{ KOH}(s) + \text{CO}_2(g) \rightarrow \text{K}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$	-189	-91
$CaCO_3(s) + 2 \text{ KOH}(s) \rightarrow K_2CO_3(s) + CaO(s) + H_2O(g)$	-20	-68
$K_2S(s) + CaCO_3(s) \rightarrow K_2CO_3(s) + CaS(s)$	-34	-52
$\mathrm{K_2CO_3(s)} + \mathrm{H_2S(g)} \rightarrow \mathrm{K_2S(s)} + \mathrm{H_2O(g)} + \mathrm{CO_2(g)}$	+143	+14
$2 \text{ KCl}(s) + \text{CaCO}_3(s) \rightarrow \text{K}_2\text{CO}_3(s) + \text{CaCl}_2(s)$	+141	+122
$Na_2SiO_3(s) + CaCO_3(s) \rightarrow Na_2CO_3(s) + CaSiO_3(s)$	+8	-16
$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + CO_2(g)$	+70	-52

Table 15: Gas and solid phase chemical reactions inside of the in situ capture gasfier

We draw the following conclusions from the equilibrium thermodynamic data listed Table 15. First, it is thermodynamically favoured for calcium oxide and calcium carbonate to chemically react with the silica-aluminates in coal ash and to lose their capability to capture either CO_2 or H_2S . Second, calcium silicate can still be used to capture strong acid gases, such as hydrogen chloride, but the preferred state of chloride in the gasifier is potassium chloride, which has been shown by previous researchers to not be catalytic [76]. Abotsi *et al.* [76] showed that potassium hydroxide, carbonate and sulfide are active catalysts, whereas potassium silicate and chloride are inactive because of their stronger ionic bonds and higher melting temperatures.

Using the data in Table 15, as well as data from HSC Chemistry 6.0 not listed in Table 15 also at 1000 K and 0.1 MPa, we've ranked the thermodynamic stability of various solid states of calcium and potassium. For calcium the ranking from least to most stable is the following: $Ca(OH)_2 < CaO < CaCO_3$

< CaS < CaSiO₃ < CaCl₂. For potassium, the ranking from least to most stable anion is slightly different than calcium: $K_2O < KOH < K_2S < K_2CO_3 < K_2SiO_3 < KCl$. And for any given anion, we found the following ranking as far as which cation was more stable: $CaCO_3 < K_2CO_3$; $K_2S < CaS$; $K_2SiO_3 < K_2SiO_3 < K_2Si$ CaSiO₃; and CaCl₂ < KCl. Therefore, for the case of thermodynamic equilibrium in the gasifier when there is more Ca than K, we can state the following: (1) carbon dioxide will first be captured by potassium before it is captured by calcium; (2) hydrogen sulfide will be capture by calcium; (3) aluminasilicates in the ash will deactivate calcium rather than potassium; and (4) chlorides in the fuel, if present, will deactivate the potassium rather than the calcium. From this information, we can conclude that, from a thermodynamic point of view, the sulfur and alumina-silicates in the coal will be able to decrease the capture capability of the catalysts; however, sulfur and alumina-silicates in the coal will not be able to convert potassium cations into a non-catalytic solid because the sulfur and alumina-silicates prefers thermodynamically to be bonded with calcium cations. Due to the degradation of the calcium oxide due to interaction with the sulfur and the alumina-silicates, there would be a limit to the number of cycles that the regenerated material can be used, and this means that a purge-stream of roughly 2-3% of the material would be have to be removed and replaced by fresh calcium carbonate. However, as we will see in the next section, if the bleed-stream is to be sold to a cement kiln, then there will likely be more stringent limitations on the number of cycles that the material can be re-used.

2.4.5 Application to co-generation of cement kiln feedstock

In this section, we elaborate on one particular application of the CaO-CaCO₃ cycle in which the bleed-stream is sold to a cement kiln as a pre-calcined feedstock. This is a particularly interesting application because selling the purge-stream exiting the regenerator to a cement kiln would provide additional revenue, create less waste, and reduce greenhouse gas emissions from the cement kiln [84]. As will be shown in this section, in such a CaO-CaCO₃ process, the major limitation on the amount of material that can be recycled will likely be set by the sulfur and ash limitations imposed by cement kilns on pre-calcined feedstock. Figure 10 illustrates what this process might look like in practice. It should be noted that the process shown is similar to a process patented by Hippo and Sheth [85] and assigned to GreatPoint Energy, Inc. (Cambridge, MA). As Figure 10 shows, the purge stream would likely occur after the regenerator because the mostly CaO purge-stream could be sold as pre-calcined feed to a cement kiln rather than placing the purge-stream after the gasifier and removing material that mostly calcium carbonate.



Figure 10: Process flow diagram of the CaO/CaCO₃ cycle with the addition of potassium hydroxides to increase reaction kinetics.

During CaO regeneration, CaS can convert into either CaO+SO₂(g) or CaSO₄, depending on the amount of oxygen supplied to the gasifier [22]. Here, we assume that enough oxygen is added to the gasifier so that the sulfur remains in the solid state as CaSO₄, and that the bleed-stream is sold as a precalcined feedstock to a cement kiln. The amount of make-up CaCO₃ and KOH (or K₂CO₃) and hence the amount of bleed-stream will be a function of the limitations on the amount of CaSO₄ and ash that a cement kiln can accept in its pre-calcined feedstock.

Weimer *et al.* [36] discussed these limitations in a manuscript on their calcium looping process, which they call lime enhanced gasification (LEGS) of brown coal, which is a process that occurs at pressures around 3.0 MPa and temperatures less than 800°C. They analyzed the amount of purge-stream required to meet requirements at typical cement kilns for <10%wt CaSO₄ and <30%wt ash, where ash here means that alumina-silicate, chloride, iron, titanium, and phosphorous composition of the solid mixture. There may also be tighter requirements of some of the individual components in the ash, such as phosphorous. Weimer *et al.* [36] analyzed the case of a German brown coal with similar ash content but higher sulfur content than the Wyodak-Anderson sub-bituminous analyzed here. They determined that meeting the sulfur requirement would require a higher purge rate than the purge rate based off of the ash limitation.

Assuming the limitations listed in Weimer et al. [36] of less than 10%wt CaSO₄ and less than 30%wt

ash as well as using the data collect in this paper, we calculated the maximum number of cycles that the catalyst/capture agent material could be reused, and hence the purge-stream fraction required. First, we calculated the case if the ash content were the limiting case. If one ignores the sulfur content, then the purge fraction of calcium oxide and hence make-up fraction of calcium carbonate should be roughly 11% of the amount of total calcium oxide going around the process. In order to meet the requirement that the silica, alumina, and iron content of the purge stream is less than 30% of the solids mixture, the calcium oxide can go through only roughly 9 cycles on average before being purged. Second, if one considers only the sulfur content, then the purge fraction of calcium oxide going around the process. Therefore, in order to meet the requirement that the CaSO₄ content of the purge stream is less than 10% of the solids mixture, the calcium oxide can only go through roughly 6 cycles on average before being purged. This means that, as in the case brown coal case studied by Weimer *et al.* [36], the sulfur limit is more restrictive than the ash limit.

An ideal fuel for such a CaO-CaCO₃ cycle would be very low in ash and sulfur content so that the bleed-stream could be sold to a cement kiln as a pre-calcined feedstock without creating large bleed-streams. This sulfur limitation is the main reason why we only collected results out to 6 cycles using the 0.6wt% sulfur Wyodak-Anderson coal, and why we did not collect data with the 2%wt sulfur Pittsburgh#8 coal.

2.5 Conclusions

We demonstrated a process for turning coal into a syngas consisting of roughly 20% methane and 80% hydrogen using alkali hydroxides and calcium oxide as both catalysts and *in situ* capture agents of acid gases, such as CO_2 and H_2S . We measured significant capture of both H_2S and CO_2 by the alkali hydroxides throughout the temperature range studied, 600°C to 900°C. As expected, the hydrocarbon composition increased with pressure; the kinetic rates increased with temperature; and the amount of CO_2 capture increased with an increasing ratio of alkali hydroxide to carbon in the coal. We compared the experimental results with chemical equilibrium simulation from HSC Chemistry. By comparing results, we can make the following conclusions: (1) The methane and ethane composition was much

higher than would be expected if the gasifier were at chemical equilibrium, implying that hydrocarbon reforming was kinetically limited; (2) There was less CO_2 capture experimentally than would be expected if the gasifier were at chemical equilibrium, implying that CO_2 capture was kinetically limited.

While the exact catalyst and capture agent composition can be tailored for specific applications, here we presented results in which calcium oxide is added at a Ca:C molar ratio of 0.5:1. Our results showed a threefold in the steam-gasification kinetic rate when small amounts of potassium hydroxide were added, along with the calcium oxide and water, at a Ca:C molar ratio of 0.5:1 to the sub-bituminous coal. The reason for the significantly improved kinetics was a combination of using an alkali hydroxide and aqueous mixing the catalyst with the coal. At a commercial scale, this would likely mean that there could be a roughly threefold decrease in the size of the gasifier compared with the case of dry mixing coal and the regenerated calcium oxide. In addition, we conducted multi-cycle studies in which the CaO was calcined by heating to 900°C and re-used in repeated CaO-CaCO₃ cycles. The increased steam-coal gasification kinetics rates for both CaO and CaO+KOH persisted even when the material was reused in six cycles of gasification and calcination. Though, the ability of the CaO to capture carbon dioxide decreased roughly 2-3% per CaO-CaCO₃ cycle.

In addition, we demonstrated 60% conversion of Pittsburgh#8 coal when there was an equal molar amount of alkali hydroxide and carbon in the coal, but with no addition of water into the system. At temperatures between 800°C and 900°C, we measured first-order steam-coal gasification rates of 2 hr⁻¹ in a fixed bed reactor while capturing significant quantities of both H₂S and CO₂, and while also generating 20% methane plus ethane in the syngas on a dry molar basis. The overall conclusion is that using a mixture of alkali hydroxide and calcium oxide is a promising route for generating a methane-rich syngas.

Chapter 3 Exergy & economic analysis of a SOFC fueled by a calcium looping coal gasifier

3.1 Introduction

Here, we analyze the case of a particular type of chemical looping gasification process in which calcium oxide is the chemical being looped between the gasifier and a calciner. To the author's knowledge, this is the first economic analysis of an *in situ* calcium looping coal gasifier. While there has been a previous economic analysis of a CaO-CaCO₃ cycle integrated into an integrated gasification combined cycle (IGCC) power plant [28], in that analysis, the CaO-CaCO₃ reactors were located outside of a conventional entrained flow coal gasifier. Here, the coal is gasified in the presence of calcium oxide and small amounts of potassium hydroxide, both of which act as catalysts and acid gas capture agents. A review of previous research into CaO-CaCO₃ gasification processes can be found in Fan *et al.* [27].

In the previous chapter, we collected experimental data on a calcium looping gasification process in which potassium hydroxide was added to the looping process in order to increase the rate of coal gasification because alkali hydroxides have been well known to be better catalysts than alkali oxides [79]. Here, our goal is to use the previous results on the gas composition and kinetics rates of a calcium looping gasifier as input into an exergy and economic analysis. The outline of this chapter is as follows: (a) overview of the calcium looping gasification process flow diagram; (b) discussion of the individual components; (c) exergy analysis; (c) economic analysis; and (d) discussion and economic comparison against alternative options.

3.2 Process flow diagram: Chemical looping gasifier with pressurized SOFC

Figure 11 shows a process flow diagram of a CaO-CaCO₃ coal gasifier integrated with a hybrid SOFC power plant system. The system can be broken down into the following main components: (a) gasifier with CaO to capture acid gases, (b) CaO regenerator, (c) syngas filter for H_2S , (d) SOFC, and (e) balance of plant, such as pumps, compressors, expander, heat exchangers and the ITM separation membranes. We later cover these topics in this order. The overall system was modeled using HSC Chemistry 6.0 (Outotec, Espoo, Finland), and then this model was exported to Excel in order to perform an economic optimization using a Visual Basic macro. The model was designed so that the following four independent parameters could be varied in order to determine which set of parameters yielded the best economic results: the SOFC pressure, current density, fuel utilization and air stoichiometric ratio.



Figure 11: Process flow diagram of the CaO-CaCO₃ coal gasifier with a pressurized SOFC

In Table 16, we show the syngas composition at four important locations in the power plant. The numbers in parentheses in Table 16 correspond to the streams as labeled in Figure 11. The syngas exiting the gasifier has a molar composition of 52% H₂, 23% H₂O, 19% CH₄, 5% CO, and 2% CO₂. This gas composition was not a function of any of the four free variables and hence stayed constant in all cases analyzed. The gas composition was determined using results from the previous chapter, plus the following changes: (a) we converted every mol of C_2H_{4-6} into two moles of CH_4 and (b) we extrapolated previous results at 2 MPa [86] to slightly higher pressures (3 MPa) than we could run experimentally by using previous results of the effect of pressure on gas composition [79]. The overall H/C ratio of the syngas was 8.7 and the overall O/C ratio was 1.2. This means that there is sufficient steam to reform the methane at the inlet, which should avoid the formation of carbon without requiring novel SOFC anodes [87, 88]. While methane is only 19% of the syngas on a molar basis, on a chemical exergy basis, the syngas is 54% CH₄, 42% H₂, and 4% CO. After the SOFC, the syngas is mostly water vapor and contains lesser amounts of carbon dioxide, hydrogen and carbon monoxide. As seen in Table 16, there is a small amount of CO₂ in the exhaust gas. This is due to the CH₄ and lesser amounts of CO and CO₂ in the syngas exiting the gasifier. The amount of CO₂ capture in the gasifier was not a free parameter in our model. While the amount of CO₂ captured could easily be increased by increasing the amount of lime in the gasifier or by sending the anode tail gas directly to the calciner, we chose a case in between the requirements to meet proposed EPA requirements on GHG emissions per kWh of electricity [89] and a case in which there was 100% CCS.

Table 16: Temperature, pressure, molar syngas composition and normalized flow exergy at important locations within power plant. The numbers in parenthesis are the stream numbers as numbered in Figure 11. The values are given at the set of free parameters that maximized the IRR. The normalized flow exergy is the flow exergy of the stream normalized by the exergy in the coal entering the power plant.

	Т	р	H_2	CO	CO ₂	H ₂ O	CH ₄	O ₂	N ₂	Normalized
	[°C]	[MPa]								Exergy
Gasifier Exit (2)	700	3	52%	5%	2%	23%	19%	0%	0%	80%
Post SOFC Anode (5)	885	0.3	16%	3%	15%	66%	0%	0%	0%	27%
Post SOFC Cathode (9)	885	0.3	0%	0%	0%	0%	0%	13%	87%	36%
Combustor (11)	1073	0.1	0%	0%	3%	13%	0%	8%	77%	57%

Here, we highlight the differences between the integrated gasification fuel cell (IGFC) system in Figure 11, and the IGFC systems designed by previous researchers. For example, Li *et al.* [29] conducted an economic analysis of a IGFC power plant system that also co-produces hydrogen. In their study, the syngas entering the SOFC was 21% H₂, 1%CO, 23% CO₂, 30% H₂O, 21%CH₄, and <1ppm H₂S. Notice that the hydrogen sulfide was removed prior to the SOFC, but that the carbon dioxide was not removed prior to the SOFC. In the Li *et al.* [29] process, the syngas was generated in a catalytic coal gasifier, as in Siefert *et al.* [90]; the H₂S was removed using a cold gas physical solvent, Selexol (UOP LLC, Des Plains, IL, U.S.A.); and the CO₂ was captured after the SOFC using a water gas shift reactor and an amine solvent, aMDEA (BASF SE, Ludwigshafen, Germany). After separating out the carbon dioxide, there was a near pure stream of hydrogen that could be sold to the market. Such a system could be placed in between streams 5 & 10, as seen in Figure 11, in order to generate a co-product stream of hydrogen to sell on the market. We did not analyze H₂ as a co-product because our design already has three products: electricity, CO₂, and pre-calcined feedstock.

In the IGFC process studied by NETL, which can be found in the following reports by Gerdes *et al.* [31, 32], Grol *et al.* [30], and Newby and Keairns [33], the carbon dioxide was not captured before the SOFC, but there was both cold gas bulk removal of H_2S using Selexol and warm gas polishing of H_2S using a bed of ZnO. After the SOFC, the anode tail gas stream was oxy-combusted and the CO₂ was separated from the water vapor by a series of cooling and compression steps.

In Figure 11 and in our previous IGFC work [90], which will be presented in the next chapter, there were at least two major differences with the IGFC systems of these other researchers discussed. First, we removed CO_2 before the SOFC so that the syngas entering the anode has as little CO and CO_2 as possible, so as to avoid carbon deposition while still sending a significant amount of methane to the fuel cell so that the methane can be internally reformed to minimize SOFC cooling requirements. Second, we removed the H_2S using a warm gas process so that we didn't have to condense out water vapor and then re-inject water vapor back into the anode gas stream before the SOFC. Removing H_2S at temperatures below the dew point of water increases system complexity, costs, and decreases the overall exergy efficiency, and for these reasons, we have chosen to remove H_2S at high temperatures. In the process flow diagram shown in Figure 11, the bulk of the H_2S and CO_2 are removed inside of the gasifier by lime, which significantly decreases the number of reactors required in the system. The following sections elaborate upon the details of each of the main components of this chemical looping gasifier integrated with a pressurized SOFC.

3.2.1 Modeling of the calcium looping coal gasifier

The CaO-CaCO₃ coal gasifier is modeled based off of the CaO acceptor process by Consol Energy developed in the 1960s-1980s [22], with the noticeable change that the gasifier is a moving-bed rather than a fluidized-bed gasifier. We model the gasifier as a moving-bed rather than a fluidized bed gasifier because (a) we have experimental results in a CaO-CaCO₃ looping fixed-bed gasifier/calciner (operated similarly to a moving-bed gasifier and a moving-bed calciner) [86]; and (b) Simbeck *et al.* [91] have published cost estimates for a Lurgi MARK IV moving-bed coal gasifier. To the author's knowledge, there is no such publicly available cost estimate for the Consol CaO-CaCO₃ fluidized bed gasifier. There has been an open debate in the coal gasification community between moving-bed, fluidized-bed, and entrained-flow gasifiers. We are not arguing here that one technology is better or worse; here, we have chosen the moving-bed gasifier because of our previously collected data and because of a moving-bed gasifier's ability to handle large size fuel particles, i.e. the gasifier was chosen so it could handle municipal solid wastes (MSW) that are likely to not be able to be ground into particle sizes that can be fluidized. As we will discuss later, adding MSW into the gasifier may be a practical way of generating electricity from MSW and improving the economics of operating the CaO-looping gasifier.

The following values and assumptions went into calculating the cost of the moving-bed gasifier. The Lurgi MARK IV gasifier has a diameter of approximately 4 meters, a height of approximately 12 meters, and usable volume of approximately 100 cubic meters. The usable volume is less than the actual volume because of the space taken up by the lock-hopper equipment at the top and bottom, as well as the moving grate near the bottom. The grate near the bottom of the vessel forces the material at the bottom of bed into the lower lock-hopper, so that the unburnt carbon, ash, and calcium carbonate can be transferred to the calcination reactor. The Lurgi moving-bed gasifier was designed to operate such that the ash in the coal does not slag. A moving grate was required in order to aid in removing materials from the gasifier and the addition of CaO into the gasifier keeps the melting point of the slag well above 700°C. For example, the melting point of CaO is 2570°C, the melting point of CaSiO₃ is 1540°C, and the melting point of CaAl₂Si₂O₈ is 1550°C. Typical ash melting temperatures are on the order of 1300°C, depending on a number of variables, including the ratio of Lewis acids to Lewis bases in the ash [92].

From our experimental results in the previous chapter operating a lab-scale, moving-bed gasifier [86], we averaged the kinetic rate from the series of tests conducted out to 6 cycles, and this yielded a

gasification kinetic rate of 2.2 hr⁻¹. This means that the e-folding decay time in the reactor is roughly 30 minutes. Since 76% of the coal is gasified in this reactor and 24% of the coal leaves the gasifier as unburnt carbon in order to be oxy-combusted in the calciner, this means that the residence time in the gasifier is roughly 40 minutes. In other words, using previously collected data on the kinetic rate along with the required coal conversion, we calculated a retention time inside the gasifier of 40 minutes. Given the size of the reactor and assuming that the reactor is 30% filled by coal and 35% filled by CaO-CaCO₃ (based off of their respective mole fractions and molar density), one can calculate that the molar flow rate of carbon into a single Lurgi gasifier would be roughly 480 mol/s of C. This equates to a coal flow rate of roughly 29,000 kg/hr for the Wyodak-Anderson sub-bituminous coal studied previously [86], which has a carbon weight percent of 69%.

From a 1983 EPRI report [91], we found cost estimates of a single Lurgi MARK IV gasifier (\$11M in 1982USD). We then converted this cost per gasifier into 2010 USD assuming CE inflation from Perry's Chemical Engineering Handbook 8th Ed. [93], yielding a value of \$25M in 2010 USD for one Lurgi Gasifier. The gasifier cost does not include coal storage & handling, "owners costs" or contingency costs. Coal handling, engineering design, piping, land, construction, and contingency will be discussed later. The scale of the plant modeled here was chosen such that there was only one Lurgi gasifier.

Variable	Value
Temperature	700 °C
Outlet gas pressure	3 MPa
Coal flow rate into the reactor	29,000 kg·hr ⁻¹
Carbon molar flow rate into the reactor	480 mol/s
CaO flow rate into the reactor	200 mol/s
COD removal	76%
Retention time inside gasifier	40 minutes
Percentage volume filled by coal	30%
Total Useful Reactor Volume	100 m^3
Total Cost (US\$ 2010)	\$25 million

Table 17: Process and economic assumptions for a moving-bed, gasifier with in situ capture of CO₂ & H₂S

3.2.2 Lime regenerator -- Calciner

The purpose of the lime regenerator (i.e. calciner) is to convert the calcium carbonate back into calcium oxide and to produce a near-pure stream of CO₂, which can then be cooled and compressed for storage underground. The lime regenerator could be operated at a range of different pressures and temperatures. Here, we model the system at 900°C and 0.1 MPa, in order to make use of the experimental results from our previous research [86]. As shown in Figure 11, a stream of pure O₂ is sent to the calciner in order to oxy-combust the un-burnt coal. In addition to combusting the coal, the oxygen can also oxidize some of the ash material; in particular, CaS could be oxidized to CaSO₄. While sulfur in coal is normally considered to be a problem, there are a few advantages to having some sulfur in the coal. First, the oxidation of calcium sulfide to calcium sulfate can provide some of the thermal energy to offset the endothermic release of CO₂. In fact, the complete oxidation of 1 mol of CaS to CaSO₄ releases enough enthalpy to offset the release of 5.5 moles of CO₂ from CaCO₃. While there is roughly 200 times more carbon than sulfur in the Wyodak-Anderson coal, fully oxidizing all of the CaS to CaSO₄ could lower the amount of unburnt carbon that needs to be combusted by roughly 25%. The second advantage of having sulfur in the coal is the following. Since CaS will oxide only after essentially all of the carbon, hydrogen and carbon monoxide have been oxidized to water vapor and carbon dioxide, this allows one to send in more oxygen than required to combust the coal without leaving oxygen in the carbon dioxide stream leaving the regenerator. The sulfide (-2) to sulfate (+6) transition effectively acts like a buffer, allowing nearly all of the H₂ and CO to be oxidized without allowing the oxygen to remain in the gas. The gas leaving the calciner will be nearly 100% CO₂+H₂O, and only ppm levels of CO, H₂, and O₂. In this analysis, however, we do not assume that any sulfur is oxidized. We instead assume that there is just enough oxygen sent to the calciner in order to combust the unburnt coal to CO_2 and H_2O .

From the experimental results in a lab-scale, moving-bed gasifier in our previous work [86], we averaged the CO_2 release kinetic rate from the series of tests conducted out to 6 cycles. This yielded a CO_2 release kinetic rate of 2.9 hr⁻¹. This means that the e-folding decay time in the reactor is roughly 20 minutes. In order to obtain near complete release of the CO_2 , we allowed the CaO to remain in the calciner for three e-folding decay times, which yielded a retention time of 60 min in this reactor. As for economic assumptions, we assumed that the calciner would be a moving-bed reactor similar to a Lurgi MARK IV gasifier. Here, however, we used a scaling factor of 0.8 to account for the fact that the calciner would be smaller in scale than the gasifier because there is a lower flow rate of material into the

calciner. Using two different cost calculations, we estimated the cost of the calciner to be \$13 million in 2010 USD. The calciner cost does not include ash storage & handling, "owners costs" or contingency costs. Ash handling, engineering design, piping, land, construction, and contingency will be discussed later. In Table 18, we summarize the thermodynamics as well as economic assumptions of the calciner. While at the commercial scale it would likely make sense to operate the calciner at higher pressures and temperatures, we chose these values of pressure and temperature in our model because we have experimental data at these values.

Table 18: Process	and economic	assumptions for	the moving-bed,	calciner to	regenerate	CaO from
CaCO ₃						

Variable	Value
Temperature	900 °C
Outlet gas pressure	0.1 MPa
Unburnt carbon flow rate in the reactor	120 mol/s
CaCO ₃ flow rate into the reactor	200 mol/s
E-folding kinetic rate for CO ₂ release	2.9 hr ⁻¹
Solids retention time inside calciner	60 min
Total Useful Reactor Volume	42 m^3
Total Cost (US\$ 2010)	\$13 million

3.2.3 Syngas cleanup

A number of non-metal, minor constituents of the syngas from the gasifier can corrode the metallic nickel in the anode of solid oxide fuel cell [94-97]. These include H_2S/COS , PH_3 , S_2/H_2Se , As/AsH_3 and SbH₃. In a typical entrained flow coal gasifier, the lowest energy state for these Column V&VI non-metals is in the gaseous state bonded to hydrogen or as a diatomic molecule. A unique characteristic of the calcium looping gasifier is that H_2S , PH_3 , H_2Se , and AsH_3 are not the lowest energy states for these Column V&VI non-metals. The lowest energy states of these elements in the gasifier are solid state species when alkali earth metals are available for bonding. These solid phases are: CaS, CaSe, Ca₃(PO₄)₂, and Ca(AsO₂)₂. The advantage of operating the coal gasifier at lower temperatures than an

entrained flow gasifier and with the addition of calcium oxide is that most of the species that could damage the anode of the SOFC remain in the solid state. In Table 19, we expand upon this statement by showing the Gibbs free energy of the reactions by which these Column V&VI non-metals can be captured by calcium oxide in the gasifier.

In order to estimate the concentration of pollutant species in the syngas and to design the downstream clean up equipment, we modeled the coal gasifier using HSC Chemistry 6.0 (Outotec, Espoo, Finland) while including a number of minor elements typically found in coal. Assuming that in the input coal there was 5000 ppmv of N, 2000 ppmv of S, and 200 ppmv of P, and 2 ppmv of Se, Ar, Cd, Sb, and Hg, our chemical equilibrium simulation calculated that the syngas contained approximately 300 ppmv NH₃(g), 10 ppmv of H₂S(g), 2 ppmv Hg(g), 30 ppbv Cd(g), 30 ppbv HCN(g), 20 ppbv H₂Se, 15 ppbv COS(g), and 1 ppbv AsH₃(g). The phosphorous is entirely captured as $Ca_3(PO_4)_2$. There are many stable solid states for cadmium, antimony and selenium, such as CdSe, CaSe, and CdS; however, as has been well documented, mercury is stable in the gaseous, un-oxidized state under reducing conditions when the temperature is above ~200-300°C [98-100]. While mercury does not interact with the Ni in the SOFC anode [94], mercury is regulated by the EPA under the Clean Air Act as a hazardous air pollutant; and therefore we have included in our cost model a filter based off of technology by TDA Research (Wheat Ridge, CO) or RTI (Research Triangle Park, NC) [101] after the syngas expander and before HX#1 (i.e. Stream 3) that removes mercury when the temperature of the syngas is around or below 300°C, but above the dew point of water vapor. It should also be noted that nitrogen, unlike other Column V non-metals, is not harmful to a Ni-YSZ anode and that ammonia is a fuel for a SOFC [102]; therefore, we did not attempt to remove ammonia or diatomic nitrogen prior to the SOFC.

In the calcium looping gasifier, the bulk of this H_2S and COS is captured, as shown in previous experiments [86]. Although, small amounts of H_2S (on the order of 10 ppm) were measured in the dry syngas existing the calcium looping gasifier. Since this is more H_2S than a typical SOFC anode can tolerate, we have placed a filter just after the gasifier in order to capture H_2S+H_2Se to below 1 ppm, as well as crack any tars that might exit the gasifier.

One way to capture the remaining H_2S species is to place a bed of iron oxides or zinc oxides sorbents at the exit of the gasifier. While both iron and zinc oxide could be used in a regenerative process to capture H_2S and release $SO_2(g)$, we focus here on zinc oxide because (a) iron oxide can interact with the hydrogen in the syngas more than zinc oxide and (b) there is a regenerative zinc oxide based sorbent being developed and currently being demonstrated at the commercial scale by Eastman

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Chemical Co. (Kingsport, TN) and RTI International (Research Triangle Park, NC) [103]. This zinc oxide fluidized-bed operates at nearly the same temperature as the exit of the gasifier. Zinc oxide is a well known capture agent for hydrogen sulfide and carbonyl sulfide, and can achieve combined sulfur concentrations below 1 ppm [104-109]. The reactions inside the zinc oxide bed and the change in Gibbs free energy for these reactions are listed in Table 19. The following are the characteristics that make zinc oxide an ideal sorbent: (a) zinc oxide will capture the pollutants (H_2S , COS, H_2Se) that can damage the SOFC anode; (b) zinc oxide will not capture or react with the main constituents of the syngas (H_2 , CH₄, CO₂); and (c) zinc oxide can be regenerated from zinc sulfide and zinc selenium.

Studies have shown that zinc sulfate will decompose around 680°C into sulfur oxide gas and zinc oxide. For this reason, the regeneration step is conducted at temperatures above 700°C. If one sends in less oxygen than would be required to make zinc sulfate, then one can avoid generating zinc sulfate, and the off-gas stream will be gaseous sulfite (SO₂) and selenite (SeO₂.) There have been multiple studies that have shown that ZnO can be regenerated from ZnS without significant formation of zinc sulfate [109-113]. For example, it has been demonstrated by Sanchez-Herva *et al.* [109] that there is minimal formation of zinc sulfate, even after 9 cycles in a ZnO-ZnS process. As also seen in Table 19, the zinc oxide should also be able to be regenerated from zinc selenide. In our model, the gaseous sulfite and selenite from the zinc oxide regenerator are sent to the calciner so that they can be captured by the lime and so that they can offset the oxygen requirement of the calciner by the amount of oxygen they consume in the zinc oxide regenerator. As seen in Table 19, CaS, CaSO₄ and CaSe are stable in the calciner. This means that essentially all of the sulfur, phosphorous, selenium, arsenic species, and cadmium that enter the process in the coal ash ultimately leave the system in the CaO bleed stream bonded to calcium, either as CaS, CdSe, CaSO₄, Ca₃(PO₄)₂, CaSe, or Ca(AsO₂)₂.

In order to estimate the capital cost of this ZnO-ZnS fluidized-bed reactor, we used a cost estimate by Nexant (San Francisco, CA.) They estimated a cost of \$42 million (2001 US\$) for a system that would remove the H₂S and COS in the syngas at a 500 MW IGCC power plant [114] down to <50 ppbv. After using a scaling exponent of 0.8 and converting this to our pressure, size, flow rate, sulfur content, and 2010 US\$, we obtained a cost estimate of \$900,000 for the cost of the ZnO-ZnS cycle reactors. The cost of this system modeled here was significantly less than for the system in the Nexant cost estimate because the H₂S composition was only 10 ppm leaving the gasifier as opposed to >1000 ppm.

Table 19: Reactions of the minor syngas constituents in the CaO-CaCO3 cycle and the ZnO-ZnS cycle.The values of Gibbs free energy were obtained using HSC Chemistry 6.0 (Outotec, Espoo, Finland.)

Reaction	ΔG
	[kJ/mol]
Gasifier (700°C)	
$H_2S(g) + CaO = CaS + H_2O(g)$	-61
$COS(g) + CaO = CaS + CO_2(g)$	-93
$H_2Se(g) + CaO = CaSe + H_2O(g)$	-5
$2 PH_3(g) + 3 CaO + 5 H_2O(g) = Ca_3(PO_4)_2 + 8 H_2(g)$	-862
$2 \text{ AsH}_3(g) + 3 \text{ H}_2\text{O}(g) + \text{CaO} = \text{Ca}(\text{AsO}_2)_2 + 6 \text{ H}_2(g)$	-205
Zinc Oxide Filter (700°C)	
$H_2S(g) + ZnO = ZnS + H_2O(g)$	-73
$COS(g) + ZnO = ZnS + CO_2(g)$	-105
$H_2Se(g) + ZnO = ZnSe + H2O(g)$	-98
$ZnO + CO_2(g) = ZnCO_3$	+93
$ZnO + H_2(g) = Zn + H_2O(g)$	+56
Zinc Oxide Regenerator (800°C)	
$ZnS + 1.5 O_2(g) = ZnO + SO_2(g)$	-362
$3 \operatorname{ZnSO}_4 + \operatorname{ZnS} = 4 \operatorname{ZnO} + 4 \operatorname{SO}_2(g)$	-233
$ZnSeO_3 = ZnO + SeO_2(g)$	-16
$ZnSe+1.5 O_2(g) = ZnO + SeO_2(g)$	-202
<u>CaO Regenerator</u> (900°C)	
$2 \operatorname{CaO} + \operatorname{O}_2(g) + 2\operatorname{SO}_2(g) = 2\operatorname{CaSO}_4$	-369
$CaS + 3 CaSO_4 = 4 CaO + 4 SO_2(g)$	+189
$2 \operatorname{CaO} + \operatorname{O}_2(g) + 2\operatorname{SeO}_2(g) = 2\operatorname{CaSeO}_4$	+108
$3CO(g) + SO_2(g) + CaO = CaS + 3CO_2(g)$	-176
$3CO(g) + SeO_2(g) + CaO = CaSe + 3CO_2(g)$	-253

Variable	Value in Regenerator
Temperature	700 °C (800 °C)
Outlet gas pressure	3 MPa (0.1 MPa)
Inlet H ₂ S concentration	10 ppm
Outlet H ₂ S concentration	0.1 ppm
Syngas molar flow rate	640 mol/s
Total Cost (US\$ 2010)	\$900,000

Table 20: Process and economic assumptions for the two-fluidized-bed reactors of the ZnO-ZnS cycle

3.2.4 Solid oxide fuel cell modeling

The syngas being sent to the SOFC is high in methane and hydrogen, and has a H₂S concentration of roughly 0.1 ppm. This appears to be an ideal fuel for a SOFC because the methane can be internally reformed within the anode [115, 116] in order to minimize the amount of thermal energy that must be carried away by the hot gases or by an external coolant. Here, we model a planar-SOFC based off of publically-available data from Rolls Royce Fuel Cell Systems [117], which has demonstrated operation of the SOFC on both hydrogen and methane. Using Equation (11) to fit the Rolls Royce data at a range of different currents, pressures, and temperatures, we were able to estimate the following values for the area specific resistance, *ASR*, and the effective electrode exchange current density, i_o^0 , as seen in Equations (12-13).

$$V = V_{OCV} - i \cdot ASR - \frac{RT}{(\alpha z) \cdot F} ln\left(\frac{i}{i_o^0} + 1\right)$$
(11)

$$ASR\left[\Omega \cdot cm^{2}\right] = 0.12 + 0.18 \cdot e^{6500 \cdot \left(\frac{1}{T} - \frac{1}{1123}\right)}$$
(12)

$$i_o^0[\mathbf{A} \cdot \mathbf{cm}^{-2}] = 0.01 \cdot p[atm] \cdot e^{-6500 \cdot \left(\frac{1}{T} - \frac{1}{1123}\right)}$$
(13)

Equation (1) gives the fuel cell voltage per cell, V, as a function of the open circuit voltage, V_{ocv} , minus the Ohmic overpotential minus the effective electrode overpotential. It should be noted that the open circuit potential is a function of the partial pressure of hydrogen and water vapor on the anode and a function of the partial pressure of oxygen on the cathode. In Equation (11), *i* is the operating current density in $[A \cdot cm^{-2}]$ and (αz) is the transfer coefficient. In Equations (12-13), *p* is the pressure of the SOFC in [atm] and *T* is the temperature of the SOFC in [K]. It should be noted that i_o^0 , is the effective overpotential of the anode and cathode combined. The *ASR* and the i_o^0 are both functions of temperature. The electrode exchange current density is also a function of pressure. In Figure 12, we show both the voltage and power density versus current density curves when the fuel cell is operating at a pressure of 200 kPa, and a temperature of 850°C.



Figure 12: Voltage and power density versus current density at a pressure of 300 kPa, and a temperature of 885°C, extrapolated from Rolls Royce Fuel Cell Systems data [117].

Here we discuss some of the key constraints and assumptions in our SOFC model. First, it should be noted that there are a number of possible free variables in a pressurized SOFC system. In our later economic analysis, we varied four of these free variables, and kept the rest of them fixed. For example, the anode side inlet temperature was constrained to be 800°C; the cathode side inlet temperature was constrained to be 750°C; and the temperature difference between the inlet and outlet air on the cathode side was constrained to be less than 150°C. In our system/economic model, there were four parameters

that could vary: pressure, current density, air stoichiometric ratios and fuel utilitization. Though, there were constraints placed on these free variables. For example, the total air stoichiometric ratio was constrained to be greater than or equal to 2.0, and the fuel utilization was constrained to be less than or equal to 80%.

In addition to these system-level assumptions, we made assumptions on the mass production costs of SOFC stacks and system using cost goals from the Department of Energy (DOE) and the Solid state Energy Conversion Alliance (SECA). Using the power densities from Gerdes et al. [31] along with the DOE/SECA goal of system costs at \$400/kW, we estimated that the SOFC stack cost would be \$1700 per m² of active area (\pm 40%); that the SOFC enclosure would be \$80·(p[atm])^{0.33} per kW generated in the SOFC (\pm 40%); that the SOFC stack lifetime was 5 yrs; that the SOFC stack replacement would be \$175 per kW generated in the SOFC (\pm 40%); and that the DC/AC inverter cost would be \$70 per kW generated in the SOFC. These cost assumptions are the same as the cost goals in our previous study on an SOFC fueled by a catalytic gasifier with ex situ H₂S and CO₂ capture [90]. We chose to separate the SOFC costs into their main components, rather than to leave the costs in [\$/kW] so that we could correctly account for the fact that costs should scale with the required active area. An approach similar to our chosen cost estimating approach was done by Piroonlerkgul et al. [118], who assumed that stack costs would increase linearly with the active area. In their 2009 report, they used a value of \$1442 per m^2 of active area. Our use of \$1700 per m^2 of active area reflects the increase in rare earth metals since 2009. We have given the stack replacement costs in "per kW" because we assume that degradation of the fuel cell depends on the total power produced from the fuel cell. This is the reason that the stack replacement costs are not given in units of "per m² of active area" as was the SOFC stack cost.

3.2.5 Balance of plant

We turn now to those pieces of equipment not covered in prior sections and discuss both the thermodynamic and cost assumptions. We first discuss standard equipment in most chemical plants and power plants. For example, we assumed the isentropic efficiency and the cost for all compressors and expanders were 85% and 200 (Power[kW]) [119]. We assumed that there was a maximum firing temperature of the combustor of 1600 K. For heat exchanger costs, we assume a cost of $1000 / m^2$ of required cross section [119]. All heat exchangers were counter-flow, and we required that, at any point along the length of the heat exchanger, the temperature difference between the hot side and cold side

We now discuss the oxygen separation process, which relies on technology still under development. Ion transport membrane (ITM) oxygen separation membranes are a technology being developing by Air Products and Chemicals, Inc. (Allentown, PA) for a variety of different chemical and power plant applications. We chose to use ITM O₂ separation membranes over cryogenic distillation methods of O₂ separation because there is a stream of high temperature air after the SOFC (~850°C) that could be sent to these ITM ceramic membranes. These membranes typically operate between 800-900°C. A cryogenic O₂ separation process relies on high pressures and low temperatures, which were the opposite of the qualities of the air in our process. The membranes rely on a gradient in the partial pressure of oxygen across the membrane. Since the partial pressure of the oxygen on the air-side of the membranes was always less than 0.1 MPa, we created a vacuum pressure on the pure-O₂ side in order to provide the driving force for oxygen separation. We kept the area of the membranes constant when varying the four free parameters listed earlier. We now discuss the cost estimates for the ITM membranes, which were the same as in Gerdes et al. [32] and our previous economic analysis of an advanced IGCC power plant with H₂ and O₂ separation membranes [90]. It should be noted that ITM membranes from O₂ separation are still not commercial technology, but that their costs can be estimated because they are composed of ceramic materials with construction costs similar to SOFC ceramic membranes. The technology readiness level (TRL) of these membranes is roughly a TRL value of 7, which means that it has been demonstrated at the pilot plant scale. A TRL value of 9 would mean that it has already been demonstrated to work at commercial scale. The upfront capital cost of ITM ceramic membranes and the reactor that surrounds the membranes was assumed to be \$1500/m² of membrane surface area. Right now, production is likely two orders of magnitude less than the production rates that would achieve the estimated \$1500/m² cost for the ITM membranes. We calculated how much area was required by using values of membrane permeance measured experimentally by Sunarso et al. [120] for mixed ionicelectric conducting ceramic membranes. Like the fuel cell ceramic membranes, we assumed that these membranes would have to be replaced every five years, and we assumed that the cost of replacement would be \$500/m² because the materials could potentially be re-used and because the reactor that holds the membranes would not require replacement.

3.3 Exergy analysis

3.3.1 Introduction

Exergy and thermo-economic analyses date back to at least the 1960s [121], and have been reviewed by El-Sayed [122]. The exergy of a system is given with respect to the temperature, pressure and composition of the Earth's atmosphere, which is not the same at different times or locations. Our assumed standard state is the following: 25° C, 0.10 MPa, and a molar gas composition of 78% N₂, 20% O₂, 2% H₂O, and 0.04% CO₂. The exergy of a system is the maximum useful work that can be generated during a process that brings the system into thermal, chemical and mechanical equilibrium with the system's environment. Exergy can exist in multiple forms, such as thermo-mechanical exergy and chemical exergy; there are also corresponding forms of exergy for kinetic, potential, and electrical energy. If ignoring the potential and kinetic exergy of the flow, the molar exergy of a substance flowing into or out of a control volume can be defined as:

$$\hat{\varepsilon} = \left(\hat{h} - \hat{h}_0\right) - T_0(\hat{s} - \hat{s}_0) + \sum_i x_i \left(\hat{\mu}_i - \hat{\mu}_{i_0}\right)$$
(14)

where \hat{h} is the molar enthalpy, T is the temperature, \hat{s} is the molar entropy, x_i is the mole fraction of species *i*, and $\hat{\mu}_i$ is the chemical potential of species *i* at standard temperature and pressure. Terms without the naught symbol are for the system, and terms with the naught symbol are for the environment. The exergy of a substance cannot be negative, and it is only equal to zero when the substance is in thermal, chemical and mechanical equilibrium with its environment. By combining the first and second laws of thermodynamics for open, steady-state processes, one obtains the exergy balance equation:

$$\dot{W}_{useful} = \sum_{i} \dot{n}_{i} \,\hat{e} + \sum_{k} \left(\frac{T_{k} - T_{0}}{T_{k}} \right) \dot{Q}_{k} - T_{0} \cdot \dot{\sigma}_{irr} \tag{15}$$

where \dot{W}_{useful} is the amount of useful mechanical and electrical work generated from the system, \dot{n}_i is the molar flow rate into or out of the control volume of component *i*, T_k is the temperature at which heat \dot{Q}_k flows out of or into the control volume, T_0 is the reference temperature of the environment, and $\dot{\sigma}_{irr}$ is the rate of entropy generation inside of the control volume due to irreversible processes. It is these irreversible processes, such as the flow of particles across gradients in temperature, pressure or chemical composition, which cause exergy destruction. When exergy is destroyed, there is a loss in the amount of useful work available that can be generated from the original exergy available to the system. The amount of exergy destruction is given by the Gouy-Stodola theorem [123]:

$$\Phi_{des} = T_0 \cdot \sigma_{irr} \tag{16}$$

where Φ_{des} is the exergy destruction and σ_{irr} is the amount of entropy generated by irreversible processes. Some of the usefulness in conducting an exergy or second law analysis, in addition to a first law analysis, are the following: (1) identification of how much potentially useful work is destroyed within processes within the plant, (2) ensuring that none of the individual idealized processes inside of the plant violate the second law of thermodynamics, and (3) ensuring that the total exergy entering the plant is equal exactly to the amount of exergy leaving the plant plus the exergy destruction inside of the plant. While a standard exergy analysis is an important check to understand where improvements in the plant might be possible, a standard exergy analysis does not include calculations of the cost and/or exergy destruction associated with building and maintaining the power plant. Therefore, while an exergy analysis is useful in estimating the cost to fuel the power plant, an exergy analysis is not a substitute for a full economic analysis of a particular power plant configuration.

3.3.2 Results

In this section, we present a breakdown of the exergy destruction, as well as the exergy leaving the system as electricity and as compressed CO_2 . In Table 21, we list the power consumed/generated as well as the exergy destruction for each of the major processes in Figure 11. In Table 21, the sum of the power consumed/generated column yields the total electricity exiting the power plant normalized by the exergy entering the system; and the sum of the exergy destruction column yields the total exergy that is destroyed inside of the system or that is effectively destroyed as it leaves the system (i.e. the exhaust air and CO_2 .) The values of power generation/consumption as well as the exergy destruction in Table 21 are given at the value of pressure, current density, air that maximized the internal rate of return on investment (IRR.) As will be shown in the next section, the values of free parameters that yielded the maximum IRR were a pressure of 300 kPa, a current density of 1.0 A/cm², an air stoichiometric ratio of 2.0, and a fuel utilization of 80%.

Table 21: Normalized power and normalized exergy destruction for the major processes in the calcium looping gasifier & SOFC system. These values are presented for the case that maximized the IRR given the assumed constraints. The conditions were the following: fuel utilization in SOFC of 80%, total air stoichiometric ratio of 2, SOFC pressure of 300 kPa, current density of 1.0 A/cm², and SOFC temperature of 885°C. Bold number = input into subsystem, Un-bold number = output of subsystem

Process Step	Power /	Exergy
	Inlet Exergy	Destruction /
		Inlet Exergy
Gasifier (1c , 2, 16)		3.4%
Venturi Nozzle & Slurry Pump (0, 1a, 17, 1b, 1c)	-0.1%	3.1%
Regenerator / Calciner (16,18,19)		5.2%
O ₂ Separation (9 ,9a,19)	-1.5%	0.5%
CO ₂ Compression System (18, 21)	-0.2%	2.7%
Compressed CO ₂ Exiting System (21)		4.6%
Exhaust Air Exiting System (15)		1.0%
Fuel Expander (2,3)	3.6%	0.3%
Air Compressor (6,7)	-9.7%	1.6%
Combustor (5 , 9a ,10)		4.2%
Exhaust Turbine (11,12)	+19.3%	1.8%
Sum of HX#1-3 (1a,1b,3,4,7,8,12,15)		4.7%
SOFC & DC/AC Converter (4,5,8,9)	48.8%	6.7%
SUM	60.2%	39.8%

As can be seen in Table 21, the SOFC was the largest source of power generation, followed by the exhaust turbine, and then the fuel expander. The air compressor was the largest source of power consumption, followed by the oxygen compressor, and then the liquid pumps. The exergy destruction in the gasifier/carbonator reactor (3.4%) was fairly small compared with an entrained flow coal gasifier [90] because there was no oxygen addition and because there were coupled CO₂ capture reactions (Δ H<0, Δ S<0) and steam-coal gasification reactions (Δ H>0, Δ S>0). The combination of reactions can

yield a case in which the Δ H, Δ S and Δ G are all close to zero. The exergy destruction of this reactor is proportional to the change in the Gibbs free energy of the reactants and products. A relatively small change in the Gibbs free energy also means that there is relatively little driving force for the reaction, which is why catalysts were used to speed up the reaction rate. The exergy destruction in the regenerator / calciner (4.2%) was fairly small but it was slightly larger than the exergy destruction in the gasifier/carbonator reactor because the Δ G was not zero (since the overall Δ S was greater than zero and the overall Δ H was equal to zero, i.e. an adiabatic reactor.) The exergy destruction in the combustor was the largest source of exergy destruction, and was almost three times larger than the exergy destruction in the SOFC, because the combustion process oxidizes the fuel without generating any of the work that could potentially be generated if the fuel were sent to a SOFC. Under the choice of free variables in Table 21, the temperature of the combustor was 1346 K (1073°C).

As seen in Table 21, the overall exergy efficiency of the power plant was 60% under the choice of free variables that maximizes the rate of return on investment. In other words, of the exergy in the coal that enters the system, 60% is converted into net AC electricity and 40% is destroyed inside the system or is effectively destroyed as the gas stream exits the system and enters the outside environment. A very similar exergy efficiency was found by Siefert et al. [90] for a pressurized SOFC system fueled by a catalytic coal gasifier, which will be presented in the next chapter of the thesis. The exergy efficiency of that system was found to be 58% under the conditions that maximized the IRR of the system. The differences here were the following: (1) Capture of CO_2 was done outside of the catalytic gasifier, whereas in this study, the CO_2 capture occurred inside of the gasifier. (2) In this case, there were constraints on the pressure because the exhaust gas was being used to feed HX#1-3. In the other study, the exhaust turbine was less constrained because the gases in the heat exchangers were being supplied thermal energy via gases exiting the CO₂ capture process. It should be noted that, depending on the choice of air stoichiometric ratio, SOFC pressure, SOFC fuel utilization, and SOFC current density, the exergy efficiency of the system in Siefert et al. [90] was between 40% and 65%. Here too, the exergy efficiency could be between 40% and 65%, depending on the choice of these four free variables. While there are a number of differences between these two IGFC systems, the exergy efficiencies at the point of maximum IRR were fairly similar, and both values of exergy efficiency much higher than traditional IGCC-CCS (roughly 32%-43%) and PCC-CCS (roughly 25% to 32%) configurations [90].

In Figure 13, we present the exergy efficiency of the pressurized SOFC fueled by the CaO-CaCO₃ chemical looping gasifier/calciner discussed in this paper. The exergy efficiency is given as a function

of the current density at a range of different values of the other free variables: pressure, fuel utilization, and air stoichiometric ratio. The exergy efficiency monotonically decreases with increasing current density for any choice of the other three variables. Cases of low exergy efficiency correspond to low pressure, low fuel utilization, and high current density. And cases of high exergy efficiency are the opposite. Another trend was that higher pressures led to high efficiencies at the same current density, but too high of a pressure could cause the system to run into a temperature constraint, which means that it cannot operate at that current density at that pressure. As seen in Figure 13, each curve does not span the full range of current density because of the various system constraints. For example, at the low end of current density, the constraint that fails is typically the requirement that the hot gas side of a heat exchanger must be 30°C higher than the cold gas side at all points along a heat exchanger. At the high end of current density, the constraint that fails is typically that the temperature difference between the cathode inlet and exit is greater than 150°C. If these constraints were loosen or tightened, then the curves in Figure 13 would necessarily expand or contract to cover a larger or smaller range of current densities.



Figure 13: Exergy efficiency of the overall CaO-CaCO₃ power plant as a function of current density for a range of different values of pressure, fuel utilization, and air stoichiometric ratio. Each curve does not span the full range of current density because of the various system constraints. U.F. is the utilization percentage of fuel, A.S. is the total air stoichiometric ratio, and p is the SOFC pressure in [atm]. Each letter links a curve to its value of U.F., A.S., and p.

Table 22: System output variables for the pressurized SOFC system fueled by a CaO-CaCO₃ chemical loop gasifier & calciner. These values are presented for the case that maximized the internal rate of return on investment and such that the flow rate of coal into the system matched the flow rate into 1 Lurgi MARK IV gasifier. The conditions were the following: fuel utilization in SOFC of 80%, total air stoichiometric ratio of 2, SOFC pressure of 300 kPa, current density of 1.0 A/cm², a carbon molar flow rate of 480 mol/s into the gasifier. The SOFC temperature was 885°C, and the SOFC Voltage was 0.70 V.

Total Power Output	143 MW
SOFC Power	116 MW
Net Brayton Cycle Power	23 MW
Fuel Expander Power	9 MW
Misc. pumps and compressors	-5 MW
Exergy Efficiency	60.4%
Carbon Input	480 mol/s
Coal Input	8.3 kg/s
CO ₂ to sequestration	335 mol/s (54 ton/hr)
CO ₂ to atmosphere	145 mol/s (23 ton/hr)
Normalized CO ₂ emissions	0.16 kg CO ₂ / kWh

While previously in this section we discussed a normalized quantity (exergy efficiency) that does not depend on the scale of the power plant, here we discuss the actual scale of the system we modeled. We created a material, energy & exergy balance sheet assuming a fixed input of 480 mol/s of a molecule with the formula $CH_{0.88}O_{0.18}$. The formula was calculated based off of the C:H:O ratio of the subbituminous coal used in prior experiments [86]. The flow rate was calculated based off of the flow rate of coal into one Lurgi MARK IV gasifier, as discussed prior. It equates with a coal flow rate of 8.3 kg/s, including the 7% by weight ash in the coal. It should be noted that a single Lurgi MARK IV gasifier at the Great Plains Project is rated for handling ~12 kg/s of lignite fuel [72]. The difference in flow rate of coal constant rather than keeping the output power constant because it greatly simplified the analysis. As seen in Table 22, at the set of free parameters described above, the total AC power output from the system was 143 MW. Most of this power is from the SOFC (116 MW) while only 23 MW of net power is produced from the combined air compressor and exhaust expander, and 9 MW of power is generated by the fuel expander. As also seen in Table 22, of the 480 mol/s of carbon that enter the gasifier in the coal, 335 mol/s end up as compressed CO₂ for underground sequestration and 145 mol/s end up as gas in the exhaust exiting the system. This equates to a normalized CO₂ emissions rate of 0.16 kg CO₂ / kWh, which is much less than the proposed U.S. EPA regulations of 0.45 kg of CO₂ per kWh of electricity generated for new power plants [124]. Though, it should be pointed out that the 145 mol/s of CO₂ could be avoided fairly easily in this process because the anode tail gas could go directly to the calciner along with O₂ from the ITM separation membranes. Because the SOFC keeps the fuel and air stream separate, there are actually a number of various configuration in which this type of IGFC could yield normalized CO₂ emission rates near zero and, hence, the value of 0.16 kg CO₂ / kWh is merely given in order to point out that GHG emission levels well below the proposed EPA regulation of 0.45 kg of CO₂ per kWh could be achieved in this system.

3.4 Economic analysis

3.4.1 Capital cost estimate

While an exergy analysis can be a useful tool to minimize the loss of work potential, an exergy analysis cannot determine the economic viability of the power plant. Since the goal of most investors is to achieve as large of a rate of return on investment as possible with as little risk as possible, an exergy analysis must also be coupled with an economic analysis, such as the net present value (NPV), levelized cost of electricity (LCOE), and/or the internal rate of return on investment (IRR). As part of our economic analysis, we conducted a Class 4 Capital Cost Estimate. According to the definition from the association for the advancement of cost engineering international (AACE), a Class 4 Capital Cost Estimate is a feasibility study conducted when: (a) project definition is 1%-15%; (b) there is a process flow diagram (PFD) and equipment lists; and (c) the expected accuracy in the cost estimate is -15% to - 30% on the low side and +20% to +50% on the high side. The capital cost estimate conducted here fits this definition because (a) we have included only the major pieces of equipment in the PFD & cost estimate, and (b) there is large uncertainty in the costs of some of the equipment that are still being

commercialized. The purpose of this study is simply to aid in the investment of future research and development, so that investments by government agencies and industry can go into those research areas that will likely yield economically-viable power plant designs with minimal environmental footprint.

In Table 23, we summarize the cost assumptions, most of which have been listed in prior sections. The costs listed in Table 23 are in units of \$ 2010 USD. Cost estimates not discussed so far are the following: (a) the vessels required to handle the coal and limestone were assumed to be equal to 50 / (System efficiency[%]) per kW of net electricity generated; (b) we assumed that we would have to build a 50 km pipeline to transport the compressed CO₂ and that it could cost 30 / (System efficiency[%]) per kW of net electricity generated; (c) we assumed that Engineering design, Piping, Land, Construction, & Contingency (EPLCC) would be equal to equipment costs (i.e. that the total capital costs would be equal to twice the total equipment costs.) The costs in (a) and (b) are listed as cost divided by system efficiency per kW because the size of these vessels and diameter of the pipeline decrease if more power is generated for the same amount of input coal and output CO₂.

There were four independent parameters that could be varied in our system: SOFC pressure, SOFC current density, SOFC utilization, and total air stoichiometric ratio. A Visual Basic macro was written to calculate the normalized capital cost, the IRR, the SOFC temperature, the cell voltage, and the exergy efficiency at a range of different values for these four independent parameters. The range consisted of the following: pressures from 100 kPa to 500 kPa in increments of 50 kPa; fuel utilization from 60% to 80% in increments of 5%; total air stoichiometric ratio from 2.0 to 4.0 in increments of 0.5; and current density from 0.1 A/cm² to 1.5 A/cm² in increments of 0.1 A/cm².

Previously, we plotted the exergy efficiency at only some of the roughly 3000 conditions analyzed. In Figure 14, we plot the normalized capital costs as a function of current density at the same set of conditions as in Figure 13. The definition of the normalized capital cost is the total capital costs divided by the net AC power produced at the power plant. Of the roughly 3000 conditions analyzed, the lowest value of normalized capital cost (~\$1900) occurred at a fuel utilization of 80%, a total air stoichiometric ratio of 2.0, a SOFC pressure of 300 kPa, and a current density 1.1 A/cm². The operating current density had a large effect on the normalized capital cost. As shown previously, the exergy efficiency was monotonically decreasing with increasing current density; the normalized capital cost was monotonically decreasing with current density until roughly 1.0 A/cm². At this current density, the normalized capital cost reached a plateau and then started to increase with current density.

Equipment	Capital Cost Estimation	Uncertainty	Reference
Lurgi Mark IV Moving-Bed	\$25,000,000	$\pm 40\%$	[91]
Gasifier			
Compressor or Expander	\$200· Power[kW]	± 30%	[119]
Heat Exchanger	\$1 per cm ² of cross sectional	± 40%	[119]
	area required		
SOFC stack cost	\$1700 per m ² of active area	$\pm 40\%$	Extrapolated
			from [31]
SOFC enclosure	$80 \cdot (p[atm])^{0.33}$	$\pm 40\%$	Extrapolated
			from [31]
SOFC Stack Replacement	\$175 per kW generated in the	± 40%	Estimated
	SOFC at years 5, 10, and 15		from [31]
DC/AC converter	\$70 per kW generated in the	± 20%	Estimated
	SOFC		from [31]
ITM Membrane Reactor	\$1500 per m ² of active area	± 40%	Estimated
			from [32]
Sulfur Polishing with ZnO-ZnS	\$900,000	± 30%	Estimated
fluidized beds			from [126]
Slurry pump & slurry Venturi	\$250,000	± 30%	Commercially
nozzle			available
Water pump & H ₂ O/CO ₂	\$850,000	± 30%	Commercially
Venturi nozzle			available
Solids Handling	\$50 / (System efficiency[%])	± 40%	Estimated
	per kW of net electricity		from [32]
50 km CO ₂ pipeline	\$30 / (System efficiency[%])	$\pm 40\%$	Estimated
	per kW of net electricity		from [125]
Engineering design, Piping,	100% of the sum of equipment		
Land, Construction, &	costs		
Contingency (EPLCC)			

Table 23: Summary of Cost Estimates for CaO Looping Gasifier integrated with SOFC system

To aid in comparison with previous economic analyses of IGFC systems, we've listed the values of the normalized capital cost of each of the main pieces of equipment in Table 24. The total sum of the main pieces of equipment was \$967/kW in 2010 \$USD. With the addition of the estimate for engineering design, piping, land, construction, and contingency (EPLCC), the capital costs for the system would be \$1934/kW with an uncertainty of -30% / +50%. The likely capital costs would be in the range of 1400-3000 \$/kW. Since the units [\$/kW] are not physical and are difficult to appreciate the significant of, we have also converted these values of [\$/kW] into the physical units of time [yr] by dividing them by the average U.S. price of electricity of base load power plants at the time that the capital costs were conducted (\$50/MWh) [127]. While this calculation does not enter into our calculation of the IRR, we have included it in order to approximate what a capital cost of \$1934/kW physically means if the capacity factor were 100% and if electricity could be sold for \$50/MWh.



Figure 14: Normalized capital cost of the overall AD-SOFC power plant as a function of current density for a range of different values of pressure, fuel utilization, and air stoichiometric ratio. The curves do not cover the full range of current density because of the various system constraints. Dollar values are in 2010 USD. U.F. = Utilization percentage of fuel, A.S. = Total air stoichiometric ratio, and p = SOFC pressure in [atm]. Each letter links a curve to its value of p, U.F., and A.S.

Table 24: Capital cost estimate of CaO-CaCO₃ looping process integrated with pressurized SOFC system at the values of independent variables that yielded the maximum value of IRR. Dollar values are given in 2010 USD. *Independent variables*: SOFC Pressure = 0.3 MPa; SOFC Current Density = $1.0 \text{ A} \cdot \text{cm}^{-2}$; Fuel Utilization = 80%; Total Air Stoichiometric ratio = 2.0. *Dependent variables*: Cell Voltage = 0.70 V, SOFC Temperature = 885° C, System Efficiency = 60%. Capital costs estimates are given in [\$/kW] and [yr], in which the \$/kW has been normalized by an electricity price of \$50/MWh.

Capital Costs	[\$/kW]	[yr]
Cathode Air Compressor	32	0.07
Cathode Exhaust Turbine	64	0.15
Syngas Expander	11	0.03
Slurry Pump & Venturi	2	0.00
CO ₂ Compressor System	6	0.01
Gasifier & Solids Handling	258	0.59
Lime Regenerator	88	0.20
CO ₂ Pipeline	50	0.11
ZnO-ZnS Reactor for H ₂ S Capture	6	0.01
SOFC, DC/AC Converter,	402	0.92
& Electrical Misc.		
O ₂ Separation & Compressor	50	0.11
Engineering design, Piping, Land,	967	2 21
Construction, & Contingency (EPLCC)		
Total	1934	4.42

It should be noted that in a previous analysis of an IGFC system [90] (next chapter), we used a slightly different methodology for calculating equipment costs, and therefore, a direct comparison between this work and the previous work is not possible. The reason for the difference is that this cost estimation was purely a bottom-up approach in which we calculated the cost of the main pieces of equipment. In the prior analysis (next chapter), we combined a "bottom-up" approach with an "analogy to similar systems" approach. In Table 7 of the previous work, the \$/kW values have a share of the

engineering design, land, construction, and contingency (ELCC) in the cost, and we added a balance of plant cost of 25% for items, such as piping and values. In our prior work, we did not calculate the gasifier costs from first principles. To estimate the costs of the fluidized-bed catalytic gasifier, we took the DOE estimated cost of GE entrained flow gasifiers in units of \$ per mol/s of carbon and added on a factor of safety of 50% to reflect that fluidized-bed gasifiers are typically more expensive than entrained flow gasifiers for the same input of coal. The estimated cost of the gasifier was significantly less in this work than in the prior work. In addition to this difference in costing methodology, we used a different SOFC V vs. *i* curve to calculate the cell voltage as a function of pressure, temperature and current density. The effect of this is that overpotential calculations in the prior work using an older V vs. *i* curve. The effect of this is that overpotential calculations in the prior work were larger than in this work, and that this had the tendency of increasing SOFC costs compared with this work. These differences partially explain why the normalized capital cost was higher in the prior work (\$2600/kW) than in this work (\$1900/kW). The lower capital cost estimate does not imply that this configuration is better than the prior configuration because of the different costing methodologies.

3.4.2 IRR analysis

Since the normalized capital cost does not include information on the reoccurring costs and sale of products, we calculated the rate of return on investment using Microsoft Excel's IRR function. The inputs in the cash-flow, time-series analysis, from which the IRR was calculated, were the following: (a) capital cost estimates, (b) fuel costs, (c) costs of make-up KOH and CaCO₃, (d) fuel cell replacement in years 5, 10, 15, (e) sale of electricity, pre-calcined feedstock, and CO₂. A cash-flow, time-series was generated at each of the roughly 3000 possible combination of different pressures, current densities, fuel utilizations and air stoichiometric ratios. The IRR was calculated in Excel by solving for the interest rate, *i* that makes the net present value (NPV) of the cash-flow time-series, C_t , equal to zero [128].

$$NPV = 0 = \sum_{t=0}^{t=N} \frac{C_t}{(1+i)^t}$$
(17)

Other than just being the interest rate that makes the NPV equal to zero, the IRR we calculated can also be understood as the average yearly rate of return on investment that an equity investor would obtain if the following are true: if the project were 100% funded with equity (i.e. no fixed interest rate bonds); if there were no inflation in prices of goods; and if the investor re-invests dividends into an exactly similar projects.

In addition to the cost assumptions discussed in previous sections, the following assumptions also went into the cash-flow, time-series analysis: (a) using prior experimental data [86], we assumed that the bleed stream would have to be 1/6th of the total solid mass leaving the calciner; (b) using recent values for materials, we assumed that the cost of make-up limestone was \$20 per ton, that the cost of the makeup catalyst was \$1000 per ton of dry 95% pure KOH, and that the bleed stream could be sold for \$40 per ton to a cement kiln as a pre-calcined feedstock; (c) we assumed that the maintenance costs were fixed at 8% of the total equipment costs per year (i.e. 4% of the total upfront capital costs per year); (d) as in the prior work [90], we assumed that the CO₂ could be sold into a CO₂ pipeline at a price of \$15/ton of CO₂ (note that we already accounted for building 50 km of pipeline to attach into the existing CO₂ pipeline); (e) and also as in the prior work [90], we assumed the following: (1) that the price of coal was \$2/GJ, (2) that the average sale price of base load electricity was \$50/MWh [129], (3) that the power plant could be constructed in two years, (4) that the total capital expenditure was split equally between the two years of construction, and (5) that the power plant would operate for 20 years with a capacity factor of 80% (i.e. generating electricity at 80% of maximum design power for 365 days a year and/or generating 100% of maximum design power for 292 days a year). These assumptions were kept the same as in the prior work so that comparisons could be made against the power plants analyzed in the prior work [90].

In Figure 15, we plot the IRR as a function of current density at the same set of conditions as in Figure 13 and Figure 14. The largest value of IRR (~6%/yr) occurred at a pressure of 0.3 MPa, a current density of 1.0 A·cm⁻², a fuel utilization of 80%, and a total air stoichiometric ratio of 2.0. This location is nearly the same as the location that minimized the normalized capital cost, except that for the normalized capital cost, the optimal current density was 1.1 A·cm⁻². Using this as the optimal location, we conducted a sensitivity analysis due to the uncertainty in the capital costs. If the capital costs were overestimated by 30%, then the IRR would be 10%/yr; and if the capital costs were underestimated by 50%, then the IRR would be 2%/yr. So, given the cost assumptions and the uncertainty in the cost assumptions, this pressurized SOFC system fed by a CaO-CaCO₃ chemical looping gasifier could potentially yield a pre-tax, inflation-adjusted IRR of 6%/yr \pm 4%/yr. Here, the uncertainty is given only for the uncertainty in equipment capital costs, not for any uncertainty in maintenance costs, fuel costs, catalyst costs, electricity sale price, lifetime or capacity factor.


Figure 15: IRR of the pressurized SOFC system fueled by a CaO-CaCO₃ chemical looping gasifier as a function of current density for a range of different values of SOFC pressure, fuel utilization, and total air stoichiometric ratio. Overall plant assumptions were: electricity sale price of \$50/MWh, 2 yr construction, 20 yr operating lifetime, capacity factor of 80%, fixed maintenance costs at 4% the total normalized capital cost each year, and SOFC stack replacement at years 5, 10 & 15. Dollar values are in 2010 US\$. U.F. = Fuel Utilization, A.S. = Total air stoichiometric ratio, and p = SOFC pressure in [atm].

In addition, we calculated whether the use of KOH to increase the gasifier kinetics was justified. We calculated that the IRR would decrease from 6%/yr to 2%/yr if KOH were not added to the gasifier. So, even though the yearly materials costs would decrease without the use of KOW, the gasifier would need to be 3 times larger, and this caused the overall IRR to decrease by 4%/yr, which justifies the use of KOH to increase gasifier kinetics.

3.4.3 Sensitivity Analysis

We now conduct a more detailed sensitivity analysis in order to determine how the IRR of the system increases or decreases with changes in the cost assumptions. First, we analyzed the case in which the SOFC stack costs and stack replacement costs were doubled compared with the goal values of 1700

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 m^2 and 175/kW, respectively. In this case, the IRR decreased from 6%/yr to 3%/yr to 0%/yr as the stack and stack replacement costs increased by 50% and 100%, respectively. We found that increasing the stack and stack replacement costs had virtually no effect on the set of values of pressure, current density, fuel utilization and air stoichiometric ratio that yielded the maximum IRR. The optimal pressure was still 0.3 MPa; the optimal current density was still 1.1 A·cm⁻²; the optimal fuel utilization was still the constrained maximum of 80%; and the optimal air stoichiometric ratio was still 2.0.

Next, we analyzed how the IRR was affected by the sale price of CO₂. Using the \$1900/kW capital cost and all of the prior assumptions, we varied the sale price of CO₂ from \$15 to \$5 to a cost of \$5 per ton of CO₂. The IRR decreased from 6%/yr to 4%/yr to 2%/yr as the price of CO₂ decreased. This means that, if the CO₂ cannot be sold into a CO₂ pipeline and must be sequestered in a saline aquifer, then this will lower the IRR from roughly 6%/yr to 2%/yr. We found that increasing the stack and stack replacement costs had a small effect on the set of values of pressure, current density, fuel utilization and air stoichiometric ratio that yielded the maximum IRR. The optimal values shifted from a pressure of 0.3 MPa to 0.35 MPa, and the optimal current density shifted from 1.1 A·cm⁻² to 1.0 A·cm⁻².

We also analyzed the case in which the fuel costs could be reduced by adding 20%-by-energycontent municipal solid waste, which lowers the fuel costs to \$1/GJ. It should be noted that this system can handle small amounts of municipal solid waste (MSW) and capture the chlorine in the plastics using the CaO in the gasifier. In the case of lowering fuel costs by adding in MSW, the IRR increased to 9%/yr from 6%/yr. In the case of doubled fuel cell costs and lowered fuel costs by adding in MSW, the IRR was 3%/yr. In all of these cases, the optimal pressures, current densities, fuel utilization, and air stoichiometric ratios remained nearly the same.

In addition, we analyzed the cases of higher and lower sale prices of electricity as well as the case of lowered capacity factors. An increase or decrease in the electricity sale price by \$10/MWh caused an increase or decrease in the IRR by approximately 4%/yr. If the average yearly capacity factor decreased from 80% to 70% to 60%, the IRR decreased from 6%/yr to 3%/yr to 0%/yr, respectively. Once again, the optimal pressures, current densities, fuel utilization, and air stoichiometric ratios remained the same.

While this is a highly non-linear system, we summarize our findings in this sensitivity analysis here and in Table 25: (a) each decrease in the CO₂ sale price by \$5/ton decreases the IRR by 1%/yr; (b) a doubling of the fuel cell capital and replacement costs decreases the IRR by 6%/yr; (c) a decrease in

the fuel costs by a \$1 yields an increase in the IRR of approximately 3%/yr; and (d) an increase in electricity sale price by \$10/MWh increases the IRR by 4%/yr. This sensitivity analysis suggests that this IGFC system may be still yield positive values of IRR even if SOFC systems can't meet DOE-SECA cost goals in the short-term, provided that it is built in a location where it can obtain high CO₂ sale prices, high electricity sale prices, and/or high MSW tipping fees. Though, in such locations, many other power plant configurations may also yield positive values of IRR.

Table 25: Sensitivity analysis results for CaO-looping gasification with a pressurized SOFC.

Parameter	Change in IRR
Sale Price of CO ₂	Every \$5 decrease in CO ₂ sale price caused a 1%/yr decrease in IRR
Fuel Cell Stack & Replacement Costs	Every 50% increase in Fuel Cell Costs caused a 3%/yr decrease in IRR
Adding 20% MSW into the coal	Increased IRR by 3%/yr (same effect as decreasing fuel cost from \$2/GJ to \$1/GJ)
Electricity Sale Price	Every \$10/MWh increase or decrease caused a 4%/yr increase or decrease
Capacity Factor	Each 10% decrease in capacity factor caused a 3%/yr decrease in IRR

3.5 Comparison with B-R combined cycle

Here, we compare the SOFC system analyzed above with a system in which the syngas from the CO_2 capture gasifier is sent to a combined Brayton-Rankine combined cycle. We did this in order to determine, at what SOFC stack cost, it will be more economically viable to send the syngas from the CaO-looping gasifier/regenerator to a SOFC than to send the syngas to a Brayton-Rankine combined cycle. The syngas from the CaO-looping gasifier would be an ideal fuel for a combined cycle because of the significant amount of methane in the fuel gas. The gas turbine would not have to be rated for operation on pure H₂.

In Figure 16, we show the process flow diagram for the CaO-looping gasifier/regenerator when integrated with a combined Brayton / Rankine Cycle. In Table 26, we present a breakdown of the

subsystems in the power plant, and quantify the power generation or loss as well as the exergy destruction in each subsystem. The numbers associated with each subsystem refer to the streams as numbered in the PFD of Figure 16. Bold numbers represent input into a given subsystem whereas number that are not bolded represent flow out of a given subsystem. The overall exergy efficiency of this system (43%) is less than the exergy efficiency when the syngas is sent to a pressurized SOFC (45%-65%, depending on the choice of independent variables.) There were no independent variables in this combined cycle power plant. The air stoichiometric ratio was fixed such that the temperature and pressure of the combustor before the gas turbine were 1600 K and 1.62 MPa. As such, there was no optimization for this configuration. We used the same values of isentropic efficiency as for the SOFC case, i.e. 85% for all compressors and turbines. The inlet temperature and pressure of the first steam turbine was 565°C, 10 MPa, and 565°C, 0.6 MPa for the steam turbine after re-heat.



Figure 16: Process flow diagram of the CaO-CaCO₃ coal gasifier integrated with a Brayton-Rankine combined cycle

Table 26: Normalized power and normalized exergy destruction for the major processes in the calcium looping gasifier & SOFC system. These values are presented for the case that maximized the IRR given the assumed constraints. The conditions in the SOFC were the following: fuel utilization of 80%, total air stoichiometric ratio of 2, pressure of 300 kPa, current density of 1.0 A/cm², and temperature of 885°C. Bold numbers = an input into a subsystem, Un-bold numbers = an output of a subsystem

Process Step	Power /	Exergy Destruction /
	Inlet Exergy	Inlet Exergy
Slurry Pump / HX#1 / Venturi / Gasifier /	-0.1%	6.5%
(2,4, 5,6d, 7, 13)		
Regenerator / Calciner (1,4,5,6)		5.2%
O ₂ Separation (1,9,22)		0.1%
CO ₂ Compressor System (6 a, 6b, 6c , 6d)	-2.4%	0.4%
Compressed CO ₂ Exiting System (7)		4.6%
Exhaust Air Exiting System (15)		1.9%
Fuel Expander (2,3)	1.0%	0.1%
Air Compressor (8,9)	-31.4%	3.7%
Combustor (3,10,23)		20.9%
Exhaust Turbine (10,11)	+56.8%	3.8%
Rankine Pump (16,17)	-0.1%	0.0%
Rankine Turbines (18,19, 20,21)	18.9%	1.6%
HRSG + Re-Heat HX (6, 6a,6b,6c,11,12,		3.2%
17 ,18, 19 ,20)		
Rankine Condenser (16,21)		5.3%
SUM	42.7%	57.3%

In order to compare the two systems, we conducted a full cash-flow, time-series analysis for this configuration, using the same economic assumptions used in the pressurized SOFC analysis, such as the same costs for compressors and turbines (200/kW of power generated or consumed), the same fuel cost (2/GJ), the same EPCC (100% above equipment costs), the same gasifier/regenerator costs, and the same sale price of electricity (50/MWh.) The overall normalized capital cost for the system was 2300/kW, which was slightly higher than the overall normalized capital costs of 1900/kW for the pressurized SOFC system. In Table 27, we present a comparison of the values of IRR for the two configurations under a range of different assumptions, such as differing capacity factors/lifetimes as well as different options for carbon dioxide sequestration. In Table 27, we also present the case in which the Brayton cycle compressor and gas turbines costs are estimated to be 100/kW, while leaving the steam turbine, CO₂ compressor, and fuel expander costs at 2200/kW. This lower value for the Brayton cycle reflects the fact that the normalized costs of compressors and turbines are lower at larger scales. In this case, the overall total normalized capital costs were 1900/kW, roughly the same as for the pressurized SOFC.

Table 27: The values of IRR [%/yr] for the pressurized SOFC and for the Brayton-Rankine combined cycle under two different assumptions for capacity factor and lifetime as well as options for carbon dioxide sequestration.

CaO-Looping Gasifier Combined with		60% Capacity Factor 30 yr Lifetime	80% Capacity Factor 20 yr Lifetime
SOFC	Sal.Seq.	-1%/yr	1%/yr
	EOR	3%/yr	6%/yr
SOFC with Double	Sal.Seq.	-7%/yr	-4%/yr
the Stack Cost	EOR	-3%/yr	0%/yr
Brayton-Rankine	Sal.Seq.	-5%/yr	-4%/yr
Combined Cycle	EOR	1%/yr	2%/yr
B-R Combined Cycle	Sal.Seq.	-2%/yr	0%/yr
w/ lower B cycle costs	EOR	4%/yr	6%/yr

As seen in Table 27, the pressurized SOFC appears to be the better option if the price of SOFC stack materials can reach $1700/m^2$ with a replacement cost of 175/kW every 5 years. If the Brayton cycle costs are lowered to 100/kW, then the values of the IRR for the two cases are nearly the same (6%/yr for EOR and ~0%/yr for Sal. Seq.) If, however, the SOFC stack costs are double the target goal, then it would make more sense to send the syngas from the CaO-looping gasifier directly to a Brayton-Rankine cycle rather than the pressurized SOFC.

Before concluding this section, it's important to further discuss the SOFC cost assumptions. Since the power density of the SOFC was 0.7 W/cm² under the optimal conditions, this means our assumption of \$1700/m² for SOFC stacks corresponds to \$243/kW, and \$175/kW every 5 years corresponds to \$1225/m² every 5 years for the replacement costs. It should also be noted that there was a cost of \$80*(p[atm])^{0.33} (\$115/kW) to seal the SOFC system, such that when the stack costs are added to the cost to seal the system and the EPCC, then the effective cost of the SOFC system in this analysis was \$715/kW during construction, and \$175/kW every five years thereafter. Since the actual, unsubsidized cost of SOFC systems are currently above \$4000/kW, we included a case in Table 27 in which the SOFC stack costs are doubled compared with DOE cost targets. If instead the stack costs are \$3400/m² (effectively \$1430/kW after 100% EPCC) with a replacement cost of \$350/kW every 5 years, then as seen in Table 27, the IRR of the CaO-looping-SOFC power plant decreases by roughly 6%/yr in all of the cases analyzed. In other words, the pressurized SOFC system could achieve a higher IRR than the Brayton-Rankine combined cycle power plant configuration only if the stack costs are roughly \$1000/kW or less, after including stack sealing and EPCC.

Given that the unsubsidized costs of SOFCs was roughly \$8000/kW when the cumulative global production were on the order of 10 MW installed and assuming the same decrease in SOFC costs as have been seen for solar cells, i.e. that installed cost is proportional to the installed capacity to the negative one third power [130], then the cost of SOFCs could decrease to \$800/kW when there is an installed capacity of ~10 GW of SOFC power plants. However, it should be noted that it will likely take decades before there is an installed capacity of 10 GW of SOFCs globally, so it should be kept in mind that the cost estimates for SOFCs stack materials represent potential reachable costs in a few decades rather than today's SOFC costs.

3.6 Conclusions

We analyzed a system that integrates a CaO-CaCO₃ chemical looping gasifier with a pressurized, solid oxide fuel cell (SOFC) and we compared this configuration with a configuration in which the syngas is sent to a Brayton-Rankine combined cycle. Both configurations generate three products: electricity, pre-calcined feedstock, and compressed carbon dioxide. The pressurized solid oxide fuel cell (SOFC) was modeled based off of the Rolls Royce SOFC. Using capital costs estimates from a variety of sources, including DOE-SECA cost goals for fuel cell systems, we conducted an economic analysis of the system at a range of different operating pressures, current densities, fuel utilizations, and air stoichiometric ratios. We calculated an internal rate of return on investment (IRR), by setting the net present value of the cash-flow, time-series equal to zero, and we varied the free parameters in order to maximize the IRR. We calculated an IRR of $6\%/yr\pm 4\%/yr$ for the system when the sale price of electricity was \$50/MWh, where the uncertainty only accounts for the uncertainty in the capital costs. We conducted a sensitivity analysis to determine the effect of changing some of the assumptions in our cost model, such as the price of the fuel cell system, the sale price of CO₂, the sale price of electricity, and the fuel price.

Our calculations suggest that this IGFC configuration is a promising way to significantly decrease the greenhouse gas emissions of both the electricity industry and the cement production industry if the cost of SOFC stacks can reach close to DOE cost targets. Further research and development is therefore warranted. However, it should be noted that further R&D is required not only to decrease the capital cost of the SOFC stack, but R&D is also required to increase the lifetime and stability of the stack. In addition to reaching SOFC stack cost targets, the systems need to reach average stack lifetime close to the DOE target of 5 yrs. While most of the equipment chosen in this power plant design configuration is capable of handling sharp changes in temperature or pressure, the SOFC and the ITM ceramic materials would likely either fail or have significant increases in area specific resistance (ASR) if there rapid changes in pressure or temperature due to system failures. Because the SOFC & ITM ceramic materials are the most likely to fail under non-planned-for operation, further R&D is also justified in increasing the durability of these materials under possible rapid changes in pressure or temperature during possible malfunction elsewhere in the system.

Chapter 4 Exergy and economic analyses of advanced IGFC-CCS and IGCC-CCS power plant configurations

4.1 Introduction

Here, we present our exergy and economic analyses of two different advanced gasification based power plants where the main product was electricity and compressed carbon dioxide. The first configuration analyzed is an advanced IGFC-CCS configuration in which a catalytic coal gasifier is coupled with a pressurized hybrid solid oxide fuel cell featuring a compressor and turbine pair that can operate at pressures between 0.2 and 0.8 MPa. The main differences with the IGFC configuration in the previous chapter is that the CO_2 is captured outside of the gasifier and that the anode tail gas is recycled back to the gasifier to provide the steam required to gasify the coal. The second configuration analyzed is similar to a conventional IGCC-CCS configuration [32, 131], but with a few noticeable changes: (1) ion transport membranes (ITM) for O_2 separation rather than cryogenic air separation; (2) warm gas sulfur removal with alkali hydroxide rather than low temperature removal using physical solvents; and (3) palladium membranes for H₂ separation from the syngas rather than low temperature removal of CO_2 from the syngas using physical solvents. For both configurations, we calculated the exergy efficiency, the internal rate of return on investment (IRR), and the levelized cost of electricity (LCOE). In the next chapter, we then compared the values of IRR and LCOE to other fossil fuel power plants.

4.2 System & exergy analysis

4.2.1 Adv. IGFC with Catalytic Gasifier and Pressurized SOFC

4.2.1.1 Description of Process Flow Diagram

We conducted an exergy analysis of a power plant design in which a catalytic coal gasifier produces a methane rich syngas. Carbon dioxide is captured from the syngas before the syngas is sent to a SOFC. In this design, the anode tail gas from the SOFC is recycled back to the catalytic gasifier. Figure 17 shows the process flow diagram for the major components of this system. We used HSC Chemistry to do both a first law balance and a material balance for the catalytic gasifier, the CO₂ capture/release reactors, and the SOFC. The gas compositions throughout the loop of Steps 4-9 are listed in Table 28 when the single pass utilization of the SOFC was 70%. Since this is a process with a recycle loop and with multiple species capable of being oxidized in the fuel cell, 'single pass fuel utilization' is defined to be equal to the amount of oxygen that crosses from the cathode to the anode divided by the amount of oxygen that would cross from the cathode to the anode if all of the H₂, CO, and CH₄ entering the anode were completely oxidized to H₂O and CO₂.

Table 28: Syngas composition throughout the loop that integrates the catalytic gasifier with the SOFC, as calculated by HSC Chemistry using Gibbs free energy minimization, when the single-pass fuel utilization was 70%.

	T [°C]	p [MPa]	H ₂	СО	CO ₂	H ₂ O	CH ₄
Gasifier Exit (4)	700	3	32%	13%	13%	34%	8%
Post CO ₂ Capture (6)	460	0.5	58%	2%	1%	15%	14%
Post SOFC Anode (7)	850	0.5	29%	6%	6%	59%	0%



Figure 17: Process Flow Diagram for Catalytic Steam Gasification Integrated with a SOFC

4.2.1.2 Catalytic Coal Gasifier

The catalytic gasifier modeled here is based off of the Exxon single-stage, fluidized bed catalytic gasifier [48, 49], in which low rank coals are slurry mixed with roughly 20%wt potassium hydroxide and carbonate. A slurry of coal, catalyst and water is pumped to the pressure of the gasifier (3 MPa) and then dried using exhaust air from the low pressure Brayton cycle. This catalytic gasifier operates adiabatically at a temperature of 700°C. The dried coal and catalyst enter the catalytic gasifier along with the anode gas recycle from the SOFC. The gasifier is operated auto-thermally, in other words, the endothermic steam-coal reactions to produce hydrogen and carbon dioxide are balanced by the exothermic reactions that create methane from hydrogen and carbon monoxide. The experimental molar methane composition of the syngas from the catalytic gasifier is often 20% on a dry basis [48, 49]. In

addition to catalyzing the steam-coal gasification reaction, the alkali catalyst also can capture acid gases, such as hydrogen sulfide [79], which simplifies the syngas cleanup steps before the SOFC.

4.2.1.3 Catalyst Regeneration

The catalyst, ash and unconsumed carbon exit the gasifier and are quenched with water. We assume that the residence time in the gasifier is such that there is only 1% unconsumed carbon compared with the initial energy content of the coal. After the catalyst, ash and unconsumed carbon are quenched with water, and soluble species will enter the aqueous phase, such as potassium carbonate, potassium sulfide and some potassium alumina-silicate species. Yeboah *et al.* [46] and Sheth *et al.* [47] have studied the effect of different catalysts on the gasification rate, and determined that when the potassium is bonded to weak anions (such as OH^- , S^{2-} and CO_3^{2-}), the kinetics rates of gasification were higher than when bonded to strong anions (such as CI^-) that are stable in gasification environments. It should be noted that, while SO_4^{2-} and NO_3^- are strong anions, they are not stable in gasification environments, leaving their alkali cation available to catalyze reactions between steam and coal. Since potassium carbonate and potassium sulfide are both water soluble and active catalysts, the water soluble catalysts can be recovered at this stage.

When alkali cations react with alumina-silicates in the coal ash, their ability to catalyze steamcoal reactions significantly decreases [132]. Since alkali cations thermodynamically prefer being chemically bonded to alumina-silicates than being bonded with carbonate anions or sulfide anions, the alkali cations must be recovered from alkali alumina-silicates in order to maintain the catalytic capability of the alkali ions. Using HSC Chemistry, we found that the following trend for the bonding preference of alkali cations under gasifier conditions: $OH^- < CO_3^{2-} \approx S^{2-} < Al_xSi_yO_z^{-2z+3x+4y} < Cl^-$. This trend is the opposite of the catalytic capability of the alkali cation [46, 47]. This means that a fraction of the soluble catalyst and all of the alkali cations attached to insoluble materials must be reactivated by conversion into alkali hydroxide or alkali carbonates.

The process originally designed by Exxon to regenerate the catalyst used significant amounts of lime (CaO) in a digestion process and yielded about 90% catalyst recovery from the char/ash [48, 49]. One option for generating the CaO required for catalyst regeneration is to use some of the CaO generated in the CaCO₃ calcination step. Using HSC Chemistry, we determined the Gibbs free energies for the relevant reactions for catalyst regeneration using hydrated lime:

$$Ca(OH)_2(s) + K_2S(aq) = CaS(s) + 2 KOH(aq)$$
 $\Delta G^{300K} = -21 kJ/mol$ (18)

$$Ca(OH)_2(s) + K_2CO_3(aq) = CaCO_3(s) + 2 KOH(aq)$$
 $\Delta G^{300K} = -68 kJ/mol$ (19)

$$Ca(OH)_{2}(s) + K_{2}Al_{x}Si_{y}O_{1.5x+2y+1}(s) = CaAl_{x}Si_{y}O_{1.5x+2y+1}(s) + 2 \text{ KOH}(aq) \quad \Delta G^{300K} < 0$$
(20)

Another option, which we model here, is an electrodialysis process in which alkali hydroxides are generated from alkali carbonates, sulfides, alumina-silicates, and chloride. Through the use of selective polymer membranes [62-64], such as Nafion® (Du Pont), and the application of an electric field, alkali hydroxides can be generated from anions in which the alkali cations are more favorable bonded. Figure 18 shows a possible schematic of a catalyst regeneration process. For simplicity, we only show the example of potassium sulfide into hydrogen sulfide and potassium hydroxide.



Figure 18: Example schematic of catalyst regeneration using electrodialysis via bipolar and cation selective membranes

The following are the relevant net reactions in the electrodialysis system:

$$2 H_2O(l) + K_2S(aq) = H_2S(aq) + 2 KOH(aq) \qquad \Delta G^{300K} = +5 kJ/mol$$
(21)

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$$2 H_2O(l) + K_2CO_3 (aq) = H_2O(l) + CO_2(g) + 2 KOH(aq) \qquad \Delta G^{300K} = +5 kJ/mol$$
(22)

$$H_2O(l) + K_2Al_xSi_yO_z(s) = Al_xSi_yO_z(s) + 2 \text{ KOH}(a) \qquad \Delta G^{300K} \approx +12 \text{ kJ/mol}$$
(23)

To determine the amount of electricity required to generate alkali hydroxides from alkali carbonates, sulfates, and alumina-silicates, we first calculated the amount of alkali species that react with sulfur and alumina-silicates in the gasifier based on the sulfur and ash content of the coal. In this paper, we assume that the coal is a low ash, low sulfur coal from Power River Basin, WY with a weight fraction of 0.5% kg·kg⁻¹ sulfur and 5% kg·kg⁻¹ alumina-silicate. We then estimate the amount of electricity consumption by multiplying the molar flow of alkali sulfides times the ΔG of Eq. (9), add this to the molar flow of alkali alumina-silicates times the ΔG of Eq. (11), and then divide this sum by an electrodialysis electrical efficiency of 40%. We chose the value of 40% because it falls within the range of the electrodialysis efficiencies measured experimentally by Nagasawa *et al.* [62].

As stated earlier, the actual consumption of electricity in the electrodialysis unit will depend both on the ash content of the coal. As will be shown in the exergy analysis section, catalyst regeneration using bipolar membrane electrodialysis consumes roughly 1% of the gross electricity generated at the power plant if a low ash, low sulfur coal is used as fuel and if the weight of the alkali carbonate catalyst is 0.2 kg for every 0.8 kg of coal used.

4.2.1.4 Carbon Dioxide Capture

There are various methods of removing carbon dioxide from coal gasification syngas [133]. Commercially available physical solvents, such as Selexol (UOP LLC) or Rectisol (Linde AG and Lurgi AG), require lowering the temperature to below the dew point of the syngas. Instead, we model a chemical capture process that leaves the temperature of the syngas close to the inlet temperature of the solid oxide fuel cell. After leaving the catalytic gasifier, the methane rich syngas goes through an expander to drop the pressure of the gas to the pressure of the SOFC. Then the gas goes to a reactor filled with magnesium and calcium oxide (MgO, CaO) in order to capture CO₂ as well as any remaining H₂S and COS in the gas stream [134]. Carbon dioxide capture occurs at a temperature of 750 $^{\circ}$ C or less,

depending on the pressure after the expander. The CO_2 is regenerated from the dolomite (MgCO₃, CaCO₃) using hot exhaust gases from the SOFC at a temperature of 1000 °C and a pressure of 0.1 MPa. After this, the carbon dioxide is cooled, compressed, cooled again, dried, and then compressed to a pressure of 15 MPa for subsequent injection into a carbon dioxide pipeline.

4.2.1.5 SOFC

The syngas leaving the CO_2 capture reactor then enters the anode of the SOFC. The SOFC is the main source of electricity generation from this power plant configuration. The SOFC is modeled using V-*i* curves at various SOFC temperatures and pressures using publically-available data from Rolls Royce Fuel Cell Systems [117]. The equation used to model the fuel cell voltage was the following:

$$V = \frac{-g_{f,H_{2O}(g)}(T,1 \ atm)}{2F} + \frac{RT}{2F} ln \left[\frac{p_{H_{2}(g)}^{anode} \cdot \left(p_{O_{2}(g)}^{cathode} \right)^{1/2}}{p_{H_{2O}(g)}^{anode}} \right] - i \cdot ASR - \frac{RT}{(\alpha z) \cdot F} ln \left(\frac{i}{i_{o}^{0}} + 1 \right)$$
(24)

The voltage, V, between the anode and the cathode is equal to the open circuit voltage minus the Ohmic overpotential minus the electrode overpotential, where *i* is the operating current density in $[A \cdot cm^{-2}]$ and (αz) is the transfer coefficient, which we assume to be equal to a value of 2 in order to estimate the electrode exchange current density, i_0^0 . The Gibbs free energy of formation of water from H₂ and O₂ as function of temperature at 1 atm, $g_{f,H2O(g)}(T, 1 \text{ atm})$, was determined using HSC Chemistry. The pressures are the average pressure along the length of the fuel cell and the units of pressure in the electrode exchange current density, i_0^0 , are both functions of temperature, and the electrode exchange current density, i_0^0 , are both functions of temperature, and the electrode exchange current density is also a function of pressure. We determined the values of *ASR* and i_0^0 by fitting publically available data from Rolls Royce Fuel Cell Systems [117]. The values of *ASR* and i_0^0 were given previously in the last chaper.

After leaving the fuel cell, as seen in Figure 17, most of the anode tail gas goes directly to HX2; however, a small portion of the tail gas is mixed with the depleted air exiting the cathode. This is effectively a bleed stream in order to prevent the build of inert gas species, such as N_2 in originally in the coal as nitrogen species, and to prevent the buildup of water vapor. It should be noted that any ammonia generated in the catalytic gasifier can be used as fuel in the solid oxide fuel cell [135, 136];

and, unlike carbon dioxide and hydrogen sulfide, ammonia is basic and would not be removed from the syngas before the syngas enters the SOFC.

Gaseous fuels like methane, ammonia and carbon monoxide are internally reformed or shifted in the anode channels of the SOFC to yield the hydrogen that reacts with oxygen ions on the anode. There have been a number of research groups that have demonstrated experimentally the capability of doped Ni-YSZ anode to reform methane and higher hydrocarbons [137-143]. For example, Shiratori *et al.* [140] experimentally demonstrated operation of a SOFC for 50 h with direct biogas using a Ni-ScSZ cermet as the anode material. While most anodes composed of pure Ni-YSZ are not tolerant to high levels of H₂S or to hydrocarbons, Yang *et al.* [142] showed that Ni-YSZ anodes doped with barium and cerium are more tolerant to both hydrogen sulfide and propane.

4.2.1.6 Brayton Cycle

Depending on the fuel cell pressure, there can be significant net power generation from the combined air compressor and exhaust turbine. In this configuration, the air is first compressed and then sent to the CO_2 capture reactor to provide the cooling required to maintain the temperature for CO_2 capture below 750°C. The air then enters the cathode of the fuel cell. After the cathode, the air combines with the portion of the anode tail gas that is not recycled back to the catalytic gasifier. This exhaust gas is combusted, raising the temperature of the exhaust to the point at which it can be heat exchanged with the magnesium and calcium carbonate exiting the CO_2 capture reactor. After HX#2, the exhaust air passes through an exhaust turbine. The isentropic efficiency of all compressors and turbines in this system was assumed to be 80%.

4.2.1.7 Exergy Analysis

We now focus on the exergy analysis on this configuration that integrates a catalytic gasifier with a pressurized fuel cell operating on a methane-rich syngas. We calculated an exergetic efficiency of 58.3% for the operating conditions listed in Table 29: catalytic gasifier pressure was 3.0 MPa; SOFC pressure was 0.5 MPa; air stoichiometric ratio was 2.0; SOFC current density was 0.5 A·cm⁻²; SOFC Voltage was 0.70 V; and SOFC single pass fuel utilization was 70%. In Table 29, we list where power is either generated or consumed as well as where exergy is destroyed in the power plant due to irreversible

processes. Our calculations in Table 29, as well as those by Li *et al.*[38], show that the system efficiency for power plants with catalytic gasification with anode recycle is near 60%.

As seen in Table 29, the largest source of exergy destruction was the CO₂ capture using a combination of calcium and magnesium oxide and the associated heat exchangers to cool or heat the solid materials. The second largest source of exergy destruction was the SOFC. The exergy destruction inside the SOFC is due to irreversible processes within the fuel cells, principally Ohmic and cathode activation losses. Using the Gouy-Stodola Theorem as presented in Equation (3), the exergy destruction of a methane fueled SOFC at constant temperature is roughly equal to the overvoltage, η , times the current times the temperature of the environment (298 K), T_o , divided by the temperature of the SOFC, T_{SOFC} , and divided by the exergy of the fuel into the power plant normalized by the fuel's reduction charge [79].

SOFC Exergy Destruction
$$[\%] \cong \frac{\eta}{1V} \cdot \frac{T_0}{T_{SOFC}}$$
 (25)

Depending on the fuel, the exergy divided by the reduction charge, i.e. the number of electrons generated if the fuel is fully oxidized on an electrode, is typically between 1.0 and 1.3 V. Given the amount of electricity generated in the SOFC, the SOFC is not a major source of exergy destruction because the temperature of the SOFC is nearly four times larger than the temperature of the environment.

The third largest source of exergy loss is the 150 bar CO_2 leaving the power plant. This high pressure is required to overcome friction in the pipeline and to overcome the pressure of a typical geologic reservoir. Here, we count the exergy required to sequester the CO_2 as exergy destruction because the pressurized carbon dioxide is not being used to generate electricity at the power plant, even though this mechanical form of exergy is used for useful purposes in the EOR case. There was only minor exergy destruction inside of the catalytic gasifier because there is no oxygen consumption inside of the catalytic gasifier. The chemical oxygen demand of the syngas leaving the gasifier is equal to the chemical oxygen of the streams entering the gasifier: coal and syngas recycle. The exergy destruction of the turbines and compressors were each 3% or less. Table 29: Exergy balance for a SOFC operating on syngas from a catalytic gasifier and anode tail gas recycle back to the catalytic gasifier. Pressure of the SOFC was 0.5 MPa; air stoichiometric ratio was 2.0; SOFC current density was 0.5 A·cm⁻²; SOFC voltage was 0.7 V; and SOFC temperature was 1123 K (850°C).

Process Step	Power / Inlet	Exergy Destruction
	Exergy	or Loss / Inlet Exergy
Air Compressor (18-19)	-12.9%	0.8%
Air Turbine (22-23)	+13.8%	1.1%
Exhaust Air (24)	+0.8%	2.3%
CO ₂ Compressor (16-17)	-1.4%	0.4%
Exhaust CO ₂ (17)		5.5%
CO ₂ Capture HX's		12.9%
(5,6,7,8,19,20,21,22)		
Catalyst Regeneration with	-0.8%	0.4%
Electrodialysis (12-14)		
Catalytic Gasifier (3,4,9,10)		3.5%
Syngas Expander (4-5)	+10.5%	0.7%
Syngas Compressor (8-9)	-13.9%	3.2%
SOFC (6-7, 20-21)	+62.3%	10.8%
SUM	58.3%	41.7%

4.2.2 Adv. IGCC with H₂&O₂ Separation Membranes

4.2.2.1 Description of Process Flow Diagram

We conducted an exergy analysis of an integrated gasification coal power plant with advanced hydrogen and oxygen separation membranes. Mass and energy balances for each of the individual reactors in the system were conducted using HSC Chemistry 6.0 (Outotec, Espoo, Finland), which also calculated the chemical equilibrium composition given input flows by minimizing the Gibbs free energy. Mass, energy and exergy balances were conducted using Cantera v1.7, which is open source software by

D.G. Goodwin. Figure 19 shows the process flow diagram for all the flows and equipment modeled for this configuration. The following sub-sections provide a description of the technologies used in the process and highlight some important technological details.



Figure 19: Process flow diagram of the IGCC-CCS process modeled. *Left*: Coal gasification & Quench *Middle*: Water gas shift and H₂ separation *Bottom*: Brayton cycle & O₂ Separation *Top Right*: Rankine cycle

4.2.2.2 Gasification

We modeled a GE entrained flow gasifier using HSC Chemistry. Coal is crushed and then mixed with water before entering a slurry pump to pressurize the slurry to 4.2 MPa. The temperature at the exit of the gasifier is 1200°C, but after the syngas cooler, the temperature is 860°C. We used a H₂O-to-carbon ratio and an O₂-to-carbon ratio in the gasifier of 0.46:1 for both H₂O and O₂, which generates a

syngas composition of 30% H₂, 48% CO, 15% H₂O, and 7% CO₂ using Gibbs free energy minimization in HSC Chemistry. In order to separate out pure oxygen for use in the gasifier, 30% of the air exiting the main Brayton cycle compressor is diverted to a heat exchanger and then sent to an Ion Transport Membrane (ITM). This oxygen separation system is sized to generate enough oxygen for the gasifier and for the oxy-combustor. The oxygen-depleted air from the O₂ ceramic membrane process is taken back through a heat exchanger and then sent to the combustor of the Brayton cycle.

4.2.2.3 Syngas quench, sulfur removal & water gas shift

After exiting the syngas cooler, the syngas is quenched with liquid water containing sodium hydroxide. The sodium hydroxide is used to capture acid gases, such as hydrogen sulfide, carbonyl sulfide, and hydrogen chloride. In order to minimize the capture of carbon dioxide in this quench reactor, the pH of the sump water is maintained at or below a value of nine. We ignore the presence of HCl in the syngas in both our exergetic and economic model, but we do include the presence of 0.5% molar composition of H₂S plus COS in the syngas for the economic model. We assume that the hydrogen sulfide and carbonyl sulfide is converted into elemental sulfur via the following reactions that occur in both the Thiopaq (Paqell, Balk, The Netherlands) and LO-CAT (Merichem, Houston, TX) processes:

$$2 \operatorname{NaOH}(aq) + H_2S(g) \rightarrow \operatorname{Na}_2S(aq) + 2H_2O(l) \qquad \Delta G^{500K} = -39 \text{ kJ/mol} (26)$$

$$2 \text{ NaOH}(aq) + \text{COS}(g) \rightarrow \text{Na}_2\text{S}(aq) + 2\text{H}_2\text{O}(l) \qquad \Delta \text{G}^{\text{SOOK}} = -85 \text{ kJ/mol} \quad (27)$$

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$$Na_2S(aq) + \frac{1}{2}O_2(g) + H_2O(l) \rightarrow 2 NaOH(aq) + S(s)$$
 $\Delta G^{300K} = -160 \text{ kJ/mol}$ (28)

After exiting the quench reactor, the syngas is saturated with water at a temperature of 250 °C, and then is sent to a bed of activated carbon to remove mercury and to remove any further H₂S in the gas stream. The syngas then enters a water gas shift (WGS) reactor at a constant temperature of 250 °C and a constant pressure of 4.2 MPa. The syngas composition exiting the WGS reactor is 54% H₂, 3% CO, 7% H₂O, and 37% CO₂, using Gibbs free energy minimization constrained to not form methane in the reactor. Since the overall water gas shift reaction is exothermic, this thermal energy is removed from the WGS reactor via heat transfer with steam in the Rankine cycle.

4.2.2.4 Hydrogen Separation

There are various methods of separating hydrogen from syngas streams using inorganic membranes [144]. This technology is still in the early stages of commercial development. Typically, palladium is used because of its high permeability for hydrogen diffusion through the solid. The palladium is normally doped with other metals, such as copper, in order to reduce the cost of the membrane and to increase the tolerance of the alloy to hydrogen sulfide poisoning [145]. We assume that the palladium alloy membranes are 100% selective for hydrogen. The flux through the membrane was estimated using data from prior research on palladium alloy membranes [146] chosen at the temperature after the syngas compressor of 726 K. The hydrogen pressure on the pure side of the membrane is assumed to be to be 0.5 MPa, yielding a normalized flux of hydrogen through the membranes of roughly 0.02 mol·m⁻²·s⁻¹. Before entering the hydrogen separation membranes, the syngas is compressed to 15 MPa in order to increase the pressure and temperature of the syngas [147]. It should be noted that such a syngas compressor is not commercial-off-the-shelf technology, and would require further research and development.

4.2.2.5 Carbon Dioxide Capture

The hydrogen-depleted stream from the palladium membrane reactor is oxy-combusted with just enough oxygen to convert all carbon monoxide into carbon dioxide and all remaining hydrogen into water vapor. The oxygen here is taken from the pure oxygen stream exiting the ITM O_2 separation membranes. After catalytic oxy-combustion so that there is no oxygen remaining in the gas stream, the gases are cooled such that they leave the heat exchanger as liquid water and supercritical carbon dioxide. The water is phase separated and recycled for use in the plant. The carbon dioxide is separated and pumped to an existing CO_2 pipeline that is assumed to be located 50 km from the power plant.

4.2.2.6 ITM Oxygen Separation

In order to increase the system efficiency and decrease the capital cost compared to an IGCC-CCS configuration with cryogenic air separation, Air Products and Chemicals, Inc. (Allentown, PA) is currently developing ion transport membranes (ITM) to provide the oxygen for the gasifier [148]. In this Adv. IGCC-CCS configuration, oxygen is separated for use throughout the process by sending the hot, compressed gas from the exit of a Brayton cycle compressor to the ITM separation reactor. We assume that the mixed ionic-electronic ceramics of the ITM are 100% selective in separating oxygen from air. This process requires temperatures between 800 °C and 900 °C, and a sizeable pressure difference [120],

yielding a normalized flux of oxygen of roughly 0.03 mol \cdot m⁻²·s⁻¹). The pressure on the air side of the membrane is the same as the pressure of the Brayton cycle turbine (1.7 MPa). We assume that the permeate pressure is 0.1 MPa, and therefore, the oxygen must be cooled and compressed to 4.2 MPa before entering the gasifier and compressed to 15.0 MPa before entering the oxy-combustor.

4.2.2.7 Brayton Cycle

The Brayton cycle turbine modeled here is the GE 9001FA model with a power output of 255.6 MW, a pressure ratio of 17.0 and a heat rate of 9757 kJ per kWh. The model assumes the plant operates two of these turbines for a total Brayton cycle power output of 511 MW. Using this publically available data on the GE 9001FA, we calculated that the isentropic efficiency of the compressor and turbine of the Brayton cycle was 86%. In the combustor, hydrogen reacts with air from the main compressor and with the depleted air from the ITM oxygen separation process. The pure hydrogen stream leaving the palladium membranes is compressed from 0.5 MPa to the pressure of the Brayton turbine combustor (1.7 MPa). The main system compressor provides approximately 235% excess air. This limits the adiabatic flame temperature of the combustor to 1430°C, the specified firing temperature for the turbine. The combusted gases pass through the vanes of the turbine and are then sent to the steam generator for the Rankine cycle.

4.2.2.8 Rankine Cycle

The main Rankine steam generator utilizes the thermal energy from the Brayton cycle exhaust, the thermal energy from the carbon capture oxy-combustion exhaust, the thermal energy from the water gas shift reactor, and the thermal energy obtained by cooling the pure oxygen stream before the gasifier. This thermal energy is used to generate the steam necessary to drive the high-pressure (HP) steam turbine. The HP turbine exhaust is sent through a portion of the steam generator to provide the reheat necessary for the intermediate pressure (IP) turbine. The exhaust of this turbine is sent directly through the low-pressure (LP) turbine. Here, we consider a GE 207FA steam turbine with a HP stage at 13 MPa / 565 °C, and an LP stage at 0.5 MPa with no reheat. We assumed an isentropic efficiency of 90% when modeling the Rankine cycle. The three stages have a total output of 459MW. The stream leaving the low-pressure turbine is sent through a condenser. The condenser cools the stream using fresh water from an assumed nearby source. It is cooled in a cooling tower before being sent back to the source. After the condenser, the stream is pumped to the high-pressure turbine pressure and sent through the steam generation heat exchanger for reuse in the Rankine cycle.

4.2.2.9 Technical Performance

As seen in Table 30, the total power output was calculated to be 808 MW. This accounts for electricity generated by the two gas turbines as well as the Rankine cycle steam turbine. It also includes plant electricity requirements for all major system loads present in the process diagram in Figure 1. This is an idealized design because pipe friction loss, stray heat loss, system support equipment, auxiliary equipment, and personnel support equipment were not accounted for and would reduce total system output; however, to offset these idealizations, we purposely operated the Rankine cycle turbines sub-optimally. For example, the power from the Rankine cycle could be improved by choosing the value of the temperature entering the HP turbine, the IP turbine and especially the LP turbine to be higher than we assumed; however, we chose these sub-optimal temperatures in order to compensate for the fact that we are not modeling the pressure drops through the heat exchangers and condensers of the Rankine cycle. Using the assumptions listed above, the power plant operates at a HHV thermal efficiency and exergetic efficiency of around 43%. For comparison, NETL's analysis of an IGCC-CCS power plant with ITM, H₂ Sep & G9FA is quite similar to the flow diagram studied here [32], in which they measured a HHV efficiency of 40%.

Table 30: System output variables for the Adv. IGCC-CCS configuration model in this report

Brayton Cycle Power Output	511 MW
Rankine Cycle Power Output	459 MW
Total Power Output	808 MW
Coal Input Rate	5,230 ton/day
CO ₂ Produced	14,640 ton/day
CO ₂ Capture Rate	14,640 ton/day
Thermal Efficiency (HHV)	43.4%
Exergetic Efficiency	42.8%

4.2.2.10 Exergy Analysis

In this section, we analyze each of the main locations of exergy destruction (irreversible entropy generation) within the power plant. Table 31 shows a list of sources for the exergy destruction, as well

as the amount of exergy leaving the power plant, normalized by the inlet exergy flow of the incoming coal. We calculated that 42.8% of the inlet exergy will leave the system as electricity, 6.2% will leave as exergy in the compressed carbon dioxide, and only 0.9% will leave as the exhaust's thermal exergy.

Table	31:	Exergy	destruction	and	exergy	output	as a	percentage	of the	e inlet	exergy	for	an	Adv
IGCC	-CC	S config	uration with	H_2 a	nd O ₂ n	nembra	ne se	paration						

Net Power Exiting	42.8%
Gasifier RC HX	19.6%
Brayton Cycle Combustor	12.4%
SC CO2 Exiting	6.2%
Steam Turbine	4.2%
WGS Reactor & RC HX	2.9%
Brayton Cycle Turbine	2.9%
Post-Brayton Cycle HX	2.1%
Syngas Quench	2.0%
Rankine Cycle Condenser	1.4%
H ₂ Membrane + H2 Compressor	1.4%
Brayton Cycle Compressor	0.9%
Exhaust Air	0.9%
O ₂ Membrane	0.2%
Rankine Cycle Pump	0.1%
SUM	100.0%

The largest sources of exergy destruction are the coal gasifier/syngas cooler section (19.6%), the combustor of the Brayton cycle (12.4%), the steam turbine (4.2%), the gas turbine (2.9%), WGS reactor with associated heat exchanger (HX) (2.9%), Post-Brayton Cycle HX (2.1%), the quench system (2.0%), the H₂ membrane separation process (1.4%), the Rankine cycle condenser (1.4%), the gas compressor (0.9%), the ITM O₂ separation membrane reactor (0.2%), and finally the Rankine Cycle Pump (0.1%). The exergy destruction in the gasifier was significant because there is an inherent mismatch between the temperature of gasification (1200 °C) and the temperature at which the heat is transferred to the steam in

the Rankine cycle (< 600 °C.) There was also significant exergy destruction in the combustor because, even though the temperature of the combustor is quite high, most of the fuel is oxidized here.

For this Adv. IGCC-CCS configuration, we did not vary any independent variables in this system because the hydrogen-fueled gas turbine was designed to operate at the maximum pressure and air stoichiometric flow ratio allowed by the materials of the gas turbine. In other words, the optimal air stoichiometric ratio occurs at a constraint boundary. This is not the case for subsequent analysis of the less mature Adv. IGFC configuration, in which there are still multiple independent variables that can be parametrically evaluated, such as single-pass fuel utilization, the air stoichiometric ratio, the SOFC pressure, and the SOFC current density.

4.3 Economic analysis

4.3.1 Methodology for economic analysis

While knowing the first or second law efficiency of a power plant is useful in estimating the costs of fueling a power plant, the first or second law efficiency can't predict the economic viability of the power plant. A detailed knowledge of the capital, fuel and labor costs are required in order to calculate a figure of merit with which to compare the power plant with other investment opportunities. One should not optimize a power plant to obtain maximum system efficiency because the fuel-to-electricity system efficiency does not account for either the cost or the irreversible generation of entropy associated with building, fueling, maintaining, and deconstructing the power plant. Therefore, in addition to the exergy analyses presented earlier, we have also conducted economic feasibility analyses for these two power plant configurations. The feasibility analyses are Class 4 capital cost estimates as defined by the Association for the Advancement of Cost Engineering International (AACE) [149]. The expected accuracy of a Class 4 capital cost estimate is -15% to -30% on the low side and +20% to +50% on the high side. This means that there will be significant uncertainty in the actual capital cost of the configurations analyzed in this study, and therefore, the capital costs detailed below should be assumed to have the level of uncertain on the order of +50% / -30%.

The goal of this capital cost estimate, as well as the LCOE/IRR analysis, is to evaluate the economic viability of future technologies that have been modeled here, such as H₂ and O₂ separation membranes, catalytic gasifiers, and pressurized SOFCs. Costs for capital, operation and maintenance were determined through cost estimations from the Integrated Environmental Control Model (IECM) [15] for commercial technology and from Gerdes *et al.* [31, 32] for pre-commercial technologies, such as O₂ and H₂ separation membranes. It should be noted, though, that the actual upfront capital cost (\$/kW) of PCC and IGCC technologies in recent years, has been up to twice the overnight capital cost (\$2007/kW) listed in the papers from which this report has derived it capital cost estimates, and may be due what is called the Averch-Johnson effect [150], i.e. that it is in a firm's rational interest to have large values of \$/kW when it is guaranteed a fixed rate of return on investment. Another reason for this difference may be due to the fact that capital cost values in the literature assume equipment production rates higher than actual production rates. While there is large uncertainty in any large-scale power plant economic analysis, the goal here is simply to help determine whether certain technologies justify further research and development. The results here should not be construed as financial advice on where to invest.

One potentially useful economic figure of merit is the levelized cost of electricity (LCOE). The LCOE includes all of the variables related to building, fueling, operating and decommissioning the power plant, and in addition, the LCOE includes the interest rate on the capital loans. A simplified equation for calculating the LCOE is given below for the case in which the capacity factor, O&M, fuel cost, and interest payments are constant with time:

LCOE =
$$\frac{M + F + P + C \cdot \left[\frac{r(1+r)^{n}}{(1+r)^{n}-1}\right] \cdot (1+r)^{t} + D \cdot \left[\frac{r}{(1+r)^{n}-1}\right]}{E}$$
(29)

where M is the yearly operations and maintenance expenditures; F is the yearly fuel expenditures; P is the yearly pollution credit expenditures; C is the upfront capital expenditures; t is the construction time, weighted to account for how funds are spent during start-up; D is the decommissioning investment expenditures; r is the discount/interest rate on the capital loans; n is the number of years the system is operational; and E is the net yearly electricity generation. In this report, we will compare the values of LCOE we calculate with the value of LCOE for other base-load power plants, as calculated by previous studies referenced above. For the LCOE analyses in this report, we use an inflation-adjusted discount rate of 7%/yr. This value was chosen because it is the suggested value for an inflation-adjust discount rate is 7%/yr, according to the U.S. Office of Management and Budget (OMB) [151]. Although, it should be noted that this OMB guideline has not been updated since 1992 and we recognize that the choice of discount rate in an economic analysis should actually reflect the risk of the project and the real rates of return on investment obtained by private or regulated power producers in the same year in which the capital, O&M, and fuel costs were estimated. Since our goal is to evaluate the merits of research and development of new technologies, we have not conducted a risk analysis and we have chosen to use the OMB suggested value of 7%/yr for the real discount rate. To make a fair comparison to other power plant configurations, the fuel price and the discount rate were chosen to be the same in all cases. It should also be noted that, when comparing values of LCOE between different types of power plants, it is important to only compare values of LCOE for projects that produce the same type of electricity output, such as peak-following, base-load, and the various types of intermittent output. Therefore, we only compare the LCOE of the Adv. IGCC-CCS and IFGC-CCS cases with other fossil energy baseload power generation plants.

The calculation of the LCOE can be more challenging than just the calculation of the system efficiency because, in addition to calculating the system efficiency, one also needs to obtain cost estimates and interest rate estimates. Cost estimates are often hard to find for emerging technologies, such as SOFCs, ITMs, and H₂ separation membranes. While there are not many cost estimates for large fuel cell systems, NETL has published some estimates for the capital costs and replacement costs for SOFC systems [30-33], for ITM [32], and for H₂ separation [32, 152]. It should be noted that the stack costs assume mass production SOFC stacks at the scale of roughly 500 MW installed capacity per year, and therefore the \$/kW of stack capital costs used in this and other reports are significantly lower than the \$/kW of current SOFC technology. Currently, production of SOFC technology is on the order of 1 MW installed capacity per year. The time until SOFC technology reaches 500 MW of installed capacity per year depends crucially on its rate of production for use on natural gas.

The other relevant figure of merit used in this paper to compare between power plant configurations is the internal rate of return on investment (IRR). The IRR is the preferred figure of merit when the sale price is known, but the discount rate is uncertain; and it is often the preferred figure of merit when there are two or more products for sale. For example, Larson *et al.* [153] used an IRR analysis to determine the economic viability of a biomass gasification process in which there were three products for sale:

steam, electricity, and liquid biofuels. The average, inflation-adjusted IRR is calculated by determining the rate of return such that the net present value (NPV) of the project equals zero.

$$NPV = 0 = \sum_{t=1}^{N} \frac{l_t}{(1+i)^t}$$
(15)

where I_t is the net income in year *t* assuming no price/cost inflation, *N* is the total lifetime of the power plant, and *i* is the inflation-adjusted rate of return. The IRR is equal to the rate of return earned on the unrecovered balance of the investment. The value of *i* such that the NPV is equal to zero yields the geometric rate of return on investment for this project, assuming that the yearly income is re-invested in projects with identical rates of return on investment. Hence, for the case of power plants, the IRR measures the exponential nature of growth in the capability to do electrical work [154]. When comparing values of IRR between different types of projects, it is important to only compare values of IRR for projects that are equally risky.

One advantage of an LCOE analysis is that the levelized capital, fuel, and labor cost can be calculated separately and summed together. Another advantage is that the LCOE analysis avoids the self-referential nature of an IRR analysis; this means that the LCOE can never yield multiple solutions. On the other hand, the advantages of an IRR analysis is that it is self-referential, which is important from a public policy perspective because the IRR measures the estimated growth on the capital invested using today's electricity prices and today's capital, labor, and fuel costs. In this report, we calculate both the LCOE (assuming a given real discount rate of 7%) and the IRR (assuming a \$50/MWh price of electricity). In subsequent sections, we list the full details behind the LCOE and IRR calculation so that other researchers can use the cost estimates, vary some of the many inputs (fuel price, discount rate, electricity price, etc...), and make economic comparisons with their own power plant designs.

4.3.2 Economic analysis of IGFC with catalytic gasifier and pressurized SOFC

The system efficiency calculated earlier for this system was one of many inputs into the economic analysis of this power plant. To do this economic analysis, we assumed a power plant with a net electrical output of 300 MW. In addition to the values of electricity sale price (\$50/MWh) and coal price (\$2/GJ), which are the same as those listed above, some of the major inputs into the economic analysis

of this power plant are listed in Table 32. Balance of plant costs were considered to be equal to 25% of total capital costs, and was not included in the Adv. IGCC-CCS configuration modelled previously because the design of the IGCC-CSS is more mature and established.

Equipment	Capital Cost Estimation	Reference
Compressor or	\$2536·(Power[kW]) ^{0.78}	Extrapolated from [119]
Expander		
Heat Exchanger	\$1 per cm ² of cross sectional area	Extrapolated from [119]
	required	
SOFC stack cost	$$1670 \text{ per m}^2 \text{ of active area}$	Extrapolated from [31, 32]
SOFC enclosure	$80 \cdot (p[bar])^{0.33}$ per kW generated in	Extrapolated from [31, 32]
	the SOFC	
SOFC Stack	\$175 per kW generated in the SOFC	Estimated from [31, 32]
Replacement	every five years	
Gasifier, Solids	\$420 / (System efficiency[%])	Extrapolated from [31, 32]
Prep/Handling, &	per kW of net electricity	
Catalyst Regeneration	generated	
50 km CO ₂ pipeline	\$60 / (System efficiency[%])	Estimated from [125]
	per kW of net electricity	
	generated	
DC/AC converter	\$70 per kW generated in the	Estimated from [31, 32]
	SOFC	
Battery	\$400/kWh of storage	Estimated from [155]

Table 32: Capital cost estimates for the Adv. IGFC configuration

The non-SOFC capital costs are listed in Table 32 as capital costs divided by the system efficiency because for many of these items, their cost decreases as the system efficiency increases. For example, both the size and cost of the gasifier island decrease as the efficiency of the power plant increases because a smaller gasifier is required to generate the same amount of net power from the plant. The SOFC cost estimates also reflect the increase in price for pressurizing a SOFC. Since to the author's

knowledge there are no published estimates of the capital costs of a fluidized bed catalytic gasifier at commercial scale, the capital cost was assumed to be 50% more expensive than the GE entrained flow gasifier from the previous configuration model when normalized by the same coal flow rate into the gasifier. The capital costs for the various pieces of equipment are listed in Table 33.

Table 33: Capital cost estimate of the power plant shown in Figure 17. SOFC Pressure = 0.5 MPa, SOFC Voltage = 0.7 V, SOFC Current Density = 0.5 A·cm⁻², Gasifier Pressure = 3 MPa, System Efficiency = 58%. Capital costs are given in [2007/kW] and in [yr] by normalizing by 50/MWh.

Capital Costs	[\$/kW]	[yr]	
Cathode Air Compressor	49	0.1	
Cathode Exhaust Turbine	51	0.1	
Syngas Expander	42	0.1	
Syngas Compressor	52	0.1	
CO ₂ Compressor	17	0.0	
Gasifier, Coal/Solid Prep,	720	1.6	
Catalyst recovery	720	1.0	
CO ₂ Capture &	120	0.2	
Regeneration	120	0.3	
SOFC, DC/AC Converter,	015	0.1	
& Electrical Misc.	915	2.1	
CO ₂ Pipelines	100	0.2	
Balance of Plant	517	1.2	
Total	2583	5.9	

The largest capital cost for this system was the SOFC system (\$915 per net kW). Of that cost, 73% is for the stacks, 16% is for the stack enclosures, 8% is for the AC/DC converter, and 3% is for a battery system that can store 4 minutes of the electricity generated at the power plant. We added the battery to the IGFC system in order to provide a fair comparison with PCC, NGCC, and IGCC systems whose gas and steam turbines can provide spinning reserve for the electrical grid. The second largest cost of the power plant was the gasifier and associated equipment (\$720 per net kW).

Using the cost estimates above and assuming yearly O&M cost estimates equal to 5% of the upfront capital costs, we also examined how the SOFC pressure affects the IRR of this power plant configuration. To do so, we accounted for the change in SOFC voltage as a function of pressure as given Eq. 12. Figure 20 shows both the exergy efficiency and the IRR of this power plant as a function of the SOFC pressure. The efficiency of the power plant at 2 bar is only roughly 40%, but at 8 bar, the efficiency is roughly 60%. Note that the efficiency is also a strong function of the current density and the air stoichiometric ratio, but we only analyzed the case of current density of $0.5 \text{ A} \cdot \text{cm}^{-2}$ and an air stoichiometric ratio of 2.



Figure 20: Exergy efficiency and internal rate of return on investment of the catalytic gasifier w/ SOFC modeled in Figure 17. The current density of the SOFC was 0.5 A·cm⁻². The air stoichiometric ratio was 2. Red curve is the IRR when the CO₂ is used for enhanced oil recovery, and the green curve is the IRR when the CO₂ is sequestered in a saline aquifer. Exergy efficiency is defined as the net power output divided by the exergy in the inlet coal. The assumed values were the following: capacity factor = 80%, lifetime = 20 yrs, electricity sale price = \$50/MWh, EOR sale price = \$15/ton CO₂, and Saline Aquifer cost = \$5/tonCO₂.

As seen in Figure 20, the value of IRR increases as a function of pressure from 0.2 MPa to 0.8 MPa (2 to 8 bar); however, after 0.5 MPa, there is minimal increase in the IRR. These diminished returns occur because the increased efficiency with greater pressures is balanced by increased capital costs associated with enclosing and sealing the SOFC at higher pressure. The main reasons why we have

presented the breakdown of the capital costs (Table 33) as well as the breakdown of the exergy destruction (Table 29) at a pressure of 0.5 MPa is that there seems to be diminishing returns above 0.5 MPa and this pressure appears to be a reasonably achievable pressure for a SOFC in the near-term because 0.6 MPa is on the high side of pressures tested on the Rolls Royce fuel cell system [156]. At a SOFC pressure of 0.5 MPa, the capital cost was \$2600/kW. Due to capital cost uncertainty, a low end of values (\$1800/kW) represents the case in which the assumed gasifier, SOFC, and balance of plant costs have been underestimated. Using this range of capital costs and a price of electricity of \$50/MWh, the IRR for the EOR case was $4\%/yr \pm 4\%/yr$, and the IRR for the saline aquifer case was $1\%/yr \pm 4\%/yr$. Using the range of capital costs and a real discount rate of 7%/yr, the LCOE for the EOR case was 52 ± 17 (\$2007/MWh), and the LCOE for the saline aquifer case was 60 ± 17 (\$2007/MWh), as summarized in Table 34.

Table 34: Summary of economic results for the Advanced IGFC-CCS configuration at a SOFC pressure of 0.5 MPa, an air stoichiometric ratio of 2.0, and a current density of 0.5 A·cm⁻². The assumed values were the following: capacity factor = 80%, lifetime = 20 yrs, EOR sale price = $15/ton CO_2$, and Saline Aquifer cost = $5/ton CO_2$.

	EOR Sequestration	Saline Sequestration
IRR at \$50/MWh	4 ± 4 (%/yr)	$1 \pm 4 (\%/yr)$
LCOE at 7% real discount rate	52 ± 17 (\$2007/MWh)	60 ± 17 (\$2007/MWh)

4.3.3 Economic analysis of IGCC with H₂ & O₂ membranes

We conducted both an IRR and a LCOE analysis of the Adv. IGCC-CCS process described earlier by making assumptions on the capital, fuel and labor costs and then creating cash-flow time-series for the project. The capital and labor costs for the entrained flow gasifier, the gas turbine, the steam turbine, and cooling towers were averaged from the values in the IECM model [15] and those from Gerdes *et al.* [31, 32]. The capital and labor estimates for the non-standard pieces of equipment were taken from a variety of sources, and will be discussed now. The estimated cost of the palladium membranes was \$4800/m² of membrane surface area [32]. The amount of area of membranes required was calculated based off the

flux of H_2 and O_2 through laboratory scale demonstrations [120, 146] of these technologies at the temperatures and pressure differences chosen for the power plant configuration. We estimated a replacement cost of \$8 million and \$10 million every five years for the palladium and ceramic membranes, respectively, based off of the cost and amount of the metals and other materials required to make in the reactor. We estimated that the cost to replace both the H_2 and O_2 membranes is \$22.30/kW every five years. We estimated that H_2S/COS capture using the Paqell process would cost \$174 million, which was based on the cost for commercial Paqell equipment, but at $1/10^{th}$ the scale [157], assuming a volume scaling factor of 0.8 for costs. The cost assumptions for capital and labor are shown in Table 35 below. These costs include the cost of the equipment plus their share of overhead, i.e. engineering, land, construction, start-up and contingency. The costs associated with the coal handling are included in the gasifier area, and the costs for 50 km of CO₂ pipeline [125] are included in the CO₂ Sale / Cost section, listed below.

Table 35. Equipment capital costs including its share of overhead. O&M costs included Fixed and Variable Costs, assuming 80% capacity factor. Design power output equals 808 MW. Saline cost equals \$5/tCO₂, and EOR Sale price equals \$15/tCO₂, where tCO₂ is metric tons of carbon dioxide generated.

(millions USD 2007)	Initial Capital Cost	Yearly O&M Costs		
		EOR (Saline Seq.)		
Air Separation Unit (ITM)	\$150	\$2		
Gasifier Area	\$500	\$65		
Particulate Control	\$10	\$2		
Sulfur Control	\$170	\$2		
WGS & H ₂ Separation	\$180	\$10		
Power Block	\$500	\$6		
Water Treatment	\$20	\$5		
Cooling Tower	\$100	\$5		
CO ₂ Sale / Cost	\$50	-\$54 (\$27)		
Total [Million \$]	\$1,680	\$43 (\$124)		
Total [\$/ kW]	\$2,079	\$53 (\$153)		

Using the cost assumptions above as well as an average price of baseload electricity of \$50/MWh in 2007 USD and fuel price of 2/GJ for low sulfur, bituminous Appalachian coal, we were able to determine the IRR of the project when the CO₂ was sequestered either into an existing oil-gas well or into a saline reservoir. In the EOR case, we assumed that the CO₂ could be sold at \$15 per metric ton of CO₂ (tCO₂), which is similar to the value of $12/tCO_2$ from Ravagnani *et al.* [158]. Whereas in the saline aquifer case, we assumed that the owners of the plant would have to pay $5/tCO_2$ to maintain and operate the new wells, which in the middle of the range of prices (2 - 7 per metric ton of CO₂) estimated by Eccles *et al.* [159]. The assumed lifetime of the plant was 25 years, operating at an 80% capacity factor, and with a two year construction time. The IRR for the EOR case is 8% per year.

At an inflation-adjusted discount rate of 7%/yr, the levelized capital costs are \$25/MWh; the maintenance cost are \$14/MWh; and the fuel cost is \$16/MWh. This yields an overall LCOE of \$58/MWh for the saline sequestration case and an overall LCOE of \$47/MWh for enhanced oil recovery. The IRR and the LCOE are both summarized below, and in addition, we include the uncertainty in the IRR and LCOE due to the +50% / -30% uncertainty in the capital cost of the power plant.

Table 36. Summary of economic results for Adv. IGCC configuration. The assumed values were the following: capacity factor = 80%, lifetime = 20 yrs, EOR sale price = $15/ton CO_2$, and Saline Aquifer cost = $5/ton CO_2$.

	EOR Sequestration	Saline Sequestration
IRR at \$50/MWh	8 ± 4 (%/yr)	3 ± 3 (%/yr)
LCOE at 7% real discount rate	47 ± 13 (\$2007/MWh)	58 ± 13 (\$2007/MWh)

4.4 Conclusions

We conducted exergy and economic analyses for two advanced coal-based power plants with CO₂ capture and sequestration. When conducting our capital cost analysis for the advanced IGCC-CCS-EOR design, we calculated a system efficiency of 43% (HHV and exergy efficiency) and a value of IRR of $8\pm4\%/yr$ (at \$50/MWh). When conducting our capital cost analysis for the advanced IGFC-CCS-EOR design, we calculated a system efficiency of 58% and a value of IRR of $4\pm4\%/yr$ (at \$50/MWh). The goal of the next chapter is to compare the values of IRR calculated in this chapter with the values of IRR calculated by previous researchers for similar systems and also to compare with IRR of different baseload, fossil fuel power plant configurations.

Chapter 5 Comparison with other fossil fuel power plant configurations

5.1 Introduction

Pulverized coal combustion (PCC) power plants generate between 40% and 50% of the total supply of electricity in the United States [160]. However, this percentage is likely to decrease in the future because of the currently low price of natural gas as well as the recent proposal to regulate the emission of greenhouse gases by the Environmental Protection Agency [161]. While the future for building new PCC power plants looks bleak, the future may not be as bleak for building advanced integrated gasification combined cycle with carbon capture and sequestration (IGCC-CCS) and advanced integrated gasification fuel cell with carbon capture and sequestration (IGFC-CCS) power plants that operate off of mixtures of coal, municipal solid waste, or petroleum coke.

Herzog [13] published in 1999 one of the first reports detailing the economic costs of carbon dioxide capture at coal power plants. Since then, there have been a number of economic analyses of advance fossil power plants with and without carbon dioxide capture, such as Johnson *et al.* [14], Rubin *et al.* [15, 16], Davison [17], Patino-Echeverri *et al.* [162], Kunze *et al.* [18], Hammond *et al.* [19], and Fischbeck *et al.* [163]. Johnson *et al.* [14] and Fischbeck *et al.* [163] have analyzed the effect of both natural gas prices and the price of carbon dioxide emissions on the economic viability of the various fossil fuel power plant configurations. There have also been numerous studies on the economic viability
of various fossil fuel power plants configuration conducted by the National Energy Technology Laboratory (NETL) and the Energy Information Administration (EIA). Some recent NETL studies on the economics of various advanced coal power plants with CCS, such as by Gerdes *et al.* [31, 32] and Grol *et al.* [30], include capital cost estimates of advanced IGFC-CCS power plant configurations. The Adv. IGCC-CCS and Adv. IGFC-CCS configurations analyzed here are similar to the configurations modeled by Gerdes *et al.* [31, 32] and Li *et al.* [29], with the main difference being that Li *et al.* [29] included the sale of both electricity and hydrogen.

Here, we compare the cost of electricity of the advanced power plants with power plant configurations analyzed in the previous chapters with configurations analyzed by previous research groups, such as Rubin *et al.* [15] and Gerdes *et al.* [31, 32]. In addition, we analyze at what price of natural gas and at what price of CO_2 emissions can advanced coal based power plants with CCS compete economically with natural gas combined cycle power plants (NGCC).

5.2 Exergy comparison with previous studies

It has been shown by Gerdes *et al.* [31, 32], Grol *et al.* [30], Shelton *et al.* [33], and Li *et al.* [29] that coal-based power plants using catalytic gasifiers and pressurized fuel cells can achieve system efficiencies of ~60% while sequestering >90% of the carbon dioxide generated at the power plant. Though, there are some notable differences in the approaches in each of the studies listed above. A few key differences between the Adv. IGFC system analyzed here and some of the Adv. IGFC systems analyzed by previous research are: (a) anode tail gas recycle back to the gasifier; (b) CO₂ capture before the SOFC; (c) no steam turbine; and (d) intermediate SOFC pressure. The SOFC pressure in other system analyses has either been 0.1 MPa or greater than 1 MPa. Here, we analyzed cases between 0.2 MPa and 0.8 MPa. We chose to capture CO₂ before the SOFC because this CO₂ capture step will reduce the chance of carbon build-up on the anode electrode and also remove the majority of any remaining sulfur species in the syngas. Since IGFC system designs vary significantly between research groups, the optimal configuration depends on the exact constraints and costs of fuel cell systems. Also, since many of the main pieces of equipment in an IGFC power plants are not commercial-off-the-shelf technology and since their performance and cost are still evolving, there is no way to definitely prove that there is an optimal configuration.

While Adv. IGFC technology is less mature and further away from a proved optimal configuration, the Adv. IGCC system modeled earlier was quite similar to the Adv. IGCC system modeled by Gerdes *et al.* [32] and Li *et al.* [29]. Although it should be noted that, in Li *et al.* [29], some of the hydrogen produced after the hydrogen separation membranes was compressed for sale rather than being combusted in the hydrogen turbine.

In addition to comparing with similarly designed advanced power plants, we also compare the system efficiency of the power plants modeled here with various conventional power plant configurations containing greater than 90% carbon capture and compression of the CO₂ to 15 MPa. Here, >90% capture and sequestration means that >90% of the carbon in the coal is captured and sequestered underground. Figure 21 shows the first law system efficiency (Net Work vs. Higher Heating Value, HHV) for a wide range of coal-fired, base-load power plants. The cases in blue are from NETL's analysis of various coal-based power plants [32]; the cases in red are from Li *et al.* [29]; and the cases in green are for the two configurations analyzed in this section.



Figure 21: First law system efficiency for various power plant configurations with greater than 90% CO₂ capture and compression to 15 MPa.

As seen in Figure 21, the system efficiency of conventional pulverized coal combustion (PCC) power plant with post-combustion carbon capture is around 27%. The system efficiency of an IGCC power plant with pre-combustion carbon capture is between 32% and 43%, depending on (a) the method of oxygen separation from air, (b) the method of separation of CO₂ from H₂, and (c) the temperature of the sulfur removal process. The system efficiency of an IGFC power plant is between 42% and 58%, depending greatly on (a) the type of gasifier, (b) the operating voltage, (c) the pressure of the SOFC, and (d) whether there is anode recycle back to the gasifier. One clear trend in the models is that the system efficiency increases when the carbon dioxide is captured at elevated pressure rather than at atmospheric pressure. Another trend is that system efficiency increases for similar configurations when a catalytic gasifier replaces a conventional entrained flow gasifier. The question we address in the next section of this report is whether the configurations with higher system efficiency are cost effective compared with more traditional PCC-CCS and IGCC-CCS configurations.

5.3 Economic comparison with previous studies

The goal of this section is to present the capital, fuel and labor estimates of various fossil fuel power plant configurations with or without capture of carbon dioxide from previous studies, such as Gerdes *et al.* [31, 32], Grol *et al.* [30], and Rubin *et al.* [15]. These configurations include pulverized coal combustion (PCC), integrated gasification combined cycle (IGCC), natural gas combined cycle (NGCC), and integrated gasification fuel cell (IGFC). We use capital, fuel and labor estimates from these previous studies, along with fuel prices and a range of possible prices of CO_2 emissions in the near term, to calculate the IRR and LCOE of various power plant configurations. We first present the cost estimates.

Table 37 and Table 38 show the first law system efficiency (%), capital costs (2007\$/MWh), construction time (yr), fixed O&M (\$/kW/yr), capacity factor (%), variable O&M (\$/MWh), fuel cost (\$/MWh), and lifetime (yr) of various fossil fuel based power plants. In addition, for the fuel cell systems listed in Table 2, there is a reoccurring cost every 5 years of \$175/kW of generation due to SOFC stack's replacement. The values of the maintenance/labor costs and fuel costs can be found in Gerdes *et al.* [31, 32], Grol *et al.* [30], and Rubin *et al.* [15]. All cost and prices estimates in this paper

are given in 2007 USD. Using these cost and lifetime estimates, we have generated the inflationadjusted IRR on investment for all of the major fossil-fuel based power plant configurations, i.e. this is the rate of return on investment assuming that all values of price and cost inflation are exactly equal, as was done in the economic analyses presented earlier in this report.

	SC PCC	SC PCC- 50%CCS	SC PCC- 90%CCS	NGCC	NGCC- 90%CCS	Std. IGCC	Std. IGCC- 50%CCS	Std. IGCC- 90%CCS	IGCC Adv 95%CCS
HHV Efficiency	39.1%	32.9%	27.2%	49.5%	37.8%	38.2%	36.2%	32.5%	40.2%
Capital Cost [\$/kW]	1575	2223	2870	600	1200	1813	2102	2390	2169
Weighted Construction Time [yr]	2	2	2	1	2	2	2	2	2
Fixed O&M [\$/kW/yr]	25	31	37	13	33	35	40	44	44
Capacity Factor	85%	80%	80%	85%	80%	80%	80%	80%	80%
Variable O&M [\$/MWh]	4.9	7.1	9.4	3.0	4.0	6.5	7.3	8.1	5.3
Lifetime [yr]	30	30	30	30	30	30	30	30	25
Fuel [\$/MWh]	17.5	20.7	25.1	27.6	36.1	17.9	18.9	21.0	17.0

Table 37: Summary of Capital, Fuel & Labor Estimates. The capital and labor estimates are from Gerdes *et al.* [31, 32] and Rubin *et al.* [15]. Fuel prices were assumed to be \$2/GJ for coal and \$4/GJ for natural gas. The assumed inflation-adjusted discount rate is used in the LCOE analysis presented in Figure 24. \$ = 2007 USD.

In Figure 22, we used the capital and labor estimates listed in Table 37 and Table 38 in order to calculate the IRR of various fossil fuel power plants with and without carbon dioxide capture. We assumed a fuel price of \$4/GJ for natural gas and \$2/GJ for coal based off of recent average prices coal and natural gas. As in the earlier economic analyses, we assumed CO_2 is sequestered in saline aquifers at a cost of \$5/t CO_2 [159] and assumed CO_2 can be sold for EOR at a price of \$15/t CO_2 [158]. Figure 24 shows similar information as Figure 22, but in Figure 24, we calculate the LCOE of the various power plant configurations and are able to differentiate between the Fuel& CO_2 costs, the O&M costs and the levelized capital costs.

	Std Gasifier, 0.1 MPa SOFC	Cat. Gasifier, 0.1 MPa SOFC	Cat. Gasifier, 1.8 MPa SOFC	Cat Gasifier, 0.5 MPa SOFC, Anode Recycle	
HHV Efficiency	42%	49%	56%	58%	
Capital Cost [\$/kW]	2135	2000	1824	2580	
Weight Construction Time [yr]	2	2	2	2	
Fixed O&M [\$/kW/yr]	61	68	68	30	
Capacity Factor	80%	80%	80%	80%	
Variable O&M [\$/MWh]	5.0	5.5	5.5	7.6	
Plant Lifetime [yr]	20	20	20	20	
Stack Replace Time [yr]	5	5	5	5	
Stack Replacement Costs [\$/kW]	175	175	175	175	
Fuel [\$/MWh]	16.1	13.9	12.2	11.8	

Table 38: Summary of capital, fuel & labor estimates for SOFC power plants in 2007 USD. The capital and labor estimates for column 1-3 are from Gerdes *et al.* [31, 32]. For comparison, column 4 shows the estimates used section 3c) for modeling an advanced IGFC-CCS power plant. Fuel price was assumed to be \$2/GJ for coal. The assumed inflation-adjusted discount rate is used in the LCOE analysis of Figure 24. \$ = 2007 USD.

In Figure 23, we used the capital and labor estimates listed in Table 37 and Table 38 in order to calculate the IRR of various fossil fuel power plants with and without carbon dioxide capture; however, in this case, we changed the assumptions for the capacity factor (to 60%) and the lifetime (to 30 yrs). Other than these changes in assumptions, the other assumptions remained the same. The overall trend is that the IRR decreases when the capacity factor is decreased to 60% (from 80%-85%) and the lifetime is increased to 30 yrs (from 20-30 yrs). In Figure 22, we have assigned lower values of capacity factor and lifetime for the systems that rely on technologies with lower TRL values. In Figure 23, all systems are assigned the same values of capacity factor and lifetime. Relative to the other systems, changing the capacity factor and lifetime did not have significant effect.



Figure 22: Internal rate of return on investment (IRR) for new fossil fuel, base load power plants.

Data in blue represents the rate of return if there is no tax for CO_2 emissions. Data in orange represents the rate of return if there is tax for emissions of \$10/tCO₂. Data in red represents the rate of return if there is tax for emissions of \$20/tCO₂. Data in green represents the rate of return if >90% of the CO₂ is sequestered in saline aquifers at a cost \$5/t CO₂. Data in grey represents the rate of return if >90% of the CO₂ is sold for enhanced oil recovery at a price of \$15/t CO₂. The fuel price for coal was assumed to be \$2/GJ_{th} and the natural gas fuel price was \$4/GJ_{th}. The sale price of electricity was assumed to be \$50/MWh, i.e. \$14/GJ_{el}. \$ = 2007 USD. Assumed capacity factors and lifetimes can be found in Tables 37 and 38.



Figure 23: Internal rate of return on investment (IRR) for new fossil fuel, base load plants.

Data in blue represents the rate of return if there is no tax for CO_2 emissions. Data in orange represents the rate of return if there is tax for emissions of \$10/tCO₂. Data in red represents the rate of return if there is tax for emissions of \$20/tCO₂. Data in green represents the rate of return if >90% of the CO₂ is sequestered in saline aquifers at a cost \$5/t CO₂. Data in grey represents the rate of return if >90% of the CO₂ is sold for enhanced oil recovery at a price of \$15/t CO₂. The fuel price for coal was assumed to be \$2/GJ_{th} and the natural gas fuel price was \$4/GJ_{th}. The sale price of electricity was assumed to be \$50/MWh, i.e. \$14/GJ_{el}. \$ = 2007 USD. Capacity factor was assumed to be 60% and the lifetimes was assumed to be 20 yrs.



Figure 24: LCOE in 2007 USD / MWh of building new fossil fuel, base load power plants.

The cost is broken down into levelized capital costs, the fixed plus variable O&M, and the sum of the cost for fuel plus CO_2 emissions or sales. 'Sal. Seq.' means sequestration in saline aquifers at a cost \$5/t CO₂. 'EOR' means enhanced oil recovery at a positive sale price of \$15/t CO₂. The fuel price for coal was assumed to be \$2/GJ_{th} and the natural gas fuel price was \$4/GJ_{th}. The assumed inflation-adjusted discount rate was 7%/yr. Assumed capacity factors and lifetimes can be found in Tables 37 and 38.

Of the power plants analyzed, NGCC power plants yield the highest rate of return on investment. Though, this would only be until the price of CO_2 emissions reaches $25/tCO_2$. At this price of CO_2 emissions, the NGCC power plant would have an IRR of 8%/yr, and this means that the following three different configurations would be equally viable and have an IRR of 8%: NGCC, advanced IGCC-CCS-EOR, and advanced IGFC-CCS-EOR that integrates a catalytic coal gasifier with a pressurized SOFC.

The IRR of a conventional IGCC-100%CCS-EOR and the other IGFC configuration would yield an IRR near 6%/yr. Many of the configurations with sequestration in a saline aquifer yield a negative rate of return on investment, including the IGCC-CCS power plant configuration with CO₂ sequestration in a saline aquifer. For the configurations with negative values of IRR, this means that more money is spent constructing the facility than is generated in total net yearly revenue. Building a new PCC-CCS power plant configuration is unlikely to be economically viable compared with the alternative options listed above; however, it should be noted that retrofitting existing coal power plants may be economically viable [164], either for carbon capture or for conversion into NGCC power plants.

Since a power plant requires a certain amount of useful physical work to be constructed, fueled, and maintained and since a power plant also generates a certain amount of useful physical work over its lifetime, what we are attempting to express in Figure 22 is the pre-tax, inflation-adjusted rate of return on useful physical work invested for various fossil-fuel power plant configurations. Whether these configurations with negative values of IRR, when using an electricity sale price of \$50/MWh, could achieve positive values of IRR at higher sale prices of electricity depends crucially on how much the capital, fuel, and labor costs for these power plants were to increase if the average price of electricity were to increase compared with the price of electricity during the time period that the original capital, fuel and labor costs were estimated. In this study, we chose a value of \$50/MWh (\$2007USD) because it reflects an average base load sale price of electricity to power producers. For example, in 2007 the average price of electricity paid by industrial customers in the US was \$64/MWh, respectively [165]. Since this value of \$64/MWh includes transportation and distribution costs, we have chosen to use the value of \$50/MWh to reflect an average base load sale price of electricity during the time period that the capital, labor, and fuel prices were calculated in this study. If the average price of electricity were to increase in the US, such that \$50/MWh were not an accurate estimate of the sale price of base load electricity, the value of IRR (in units of %/yr) could still remain the same if the percent increase in electricity prices were the same as the percent increase in capital, fuel and labor costs.

We now compare the values of IRR calculated for the Adv. IGCC-CCS and Adv. IGFC-CCS configurations analyzed in detail earlier in this paper to the IRR of the configurations in Figure 22. The IRR for the Adv. IGCC-CCS-EOR configuration was 8 ± 4 [%/yr] and the IRR for the Adv. IGCC-CCS-Sal.Seq. configuration was 3 ± 3 [%/yr]. These values are similar to the values of 8%/yr and 2%/yr, respectively, obtained using lumped cost estimates from Gerdes *et al.* [31, 32] for an IGCC-CCS configuration with H₂&O₂ separation membranes and a gas turbine operating solely on hydrogen fuel.

The similarity is due to the fact that the designs were quite similar, and the cost estimates for the gasifier and turbines from the IECM are similar to or are the same as the values used by Gerdes *et al.* [31]. The IRR for the Adv. IGFC-CCS-EOR configuration was 4 ± 4 [%/yr] and the IRR for the Adv. IGFC-CCS-Sal.Seq. configuration was 1 ± 4 [%/yr]. These values are similar to the values of 8%/yr and 1%/yr, respectively, obtained using lumped cost estimates by Gerdes *et al.* [31, 32] for an IGFC-CCS configuration with a catalytic gasifier and a pressurized SOFC. Though it should be noted that there were some major differences between the IGFC configuration in Gerdes *et al.* [31, 32] and the one presented here. For example, in the Gerdes *et al.* [31, 32] model there was no anode tail gas recycle and CO₂ capture was accomplished via oxy-combustion of the anode tail gas. In addition, Gerdes *et al.* [31, 32] assumed that the catalytic gasifier costs were same as an entrained flow gasifier when normalized by the flow rate of coal into the gasifier, whereas we assumed that the catalytic gasifier was 50% more expensive per flow rate of coal. This last assumption is one reason why our capital cost estimate of the Adv. IGFC-CCS configuration (\$2583/kW) is higher than the capital cost estimate from Gerdes *et al.* [31, 32] (\$1824/kW), as listed in Table 38.

In Figure 25, we have separated out those power plants configurations shown in Figure 24 that have a value of LCOE of roughly \$50/MWh or less at a real discount of 7%/yr and that meet the EPA's proposed rule of 0.45 kg (1 lb) of CO₂ per gross kWh of electricity generated [166], which was released on March 27, 2012. These configurations, in order of least cost to highest cost, are NGCC, Adv. IGCC-100%CCS-EOR, IGCC-50%CCS-EOR, Adv. IGFC-100%CCS-EOR (18 bar SOFC), PCC-50%CCS-EOR, NGCC-100%CCS-EOR, Std. IGCC-100%CCS-EOR, and Adv. IGFC-100%CCS-EOR (1 bar SOFC). At a price of natural gas of \$4/GJ, the NGCC configuration has the lowest price of electricity. At a price of natural gas near \$6/GJ, the LCOE of the NGCC power plant will be equal to the LCOE of the Adv. IGCC-100%CCS-EOR configuration. It should be noted that we have not analyzed any power plant retrofit configurations, and therefore, the conclusions listed above only pertain to the economics of building new power plant constructions. In the next section, we analyze the case of varying both the prices of natural gas and the prices of CO₂ emissions.



Figure 25: LCOE in 2007 USD / MWh of building new fossil fuel, base load power plants.

The configurations above meet proposed EPA regulations of 0.45 kg (1 lb) of CO₂ per kWh of electricity generated. The cost is broken down into levelized capital costs, the fixed plus variable O&M, and the sum of the cost for fuel plus CO₂ EOR sales at $15/tCO_2$. The fuel price for coal was assumed to be $2/GJ_{th}$ and the natural gas fuel price was $4/GJ_{th}$. The inflation adjusted discount rate was assumed to be 7%/yr. Capital and O&M cost estimates and the assumed capacity factors and lifetimes can be found in Tables 37 and 38.

5.4 Varying the price of natural gas and CO₂ emissions

The results presented in Figure 22 suggest that the IRR of an advanced IGCC-CCS power plant is similar to the IRR of an advanced IGFC-CCS if the catalytic gasifier costs are the similar to the cost of an entrained flow gasifier for similar input of coal and if SOFC technology can achieve mass production

cost targets. However, the values of IRR calculated for these advanced power plant configurations were well below the IRR of a NGCC power plant with today's fuel prices and no CO_2 tax. We now address the following question: at what price of natural gas and at what price of CO_2 emissions would an advanced IGCC-CCS-EOR or IGFC-CCS-EOR power plant configuration be economically viable? We therefore conducted an LCOE analysis for the various power plant configurations as a function of the price of natural gas and carbon dioxide emissions, holding all other variables constant.

Figure 26 and Figure 27 show which fossil fuel power plant configuration has the lowest LCOE as a function of the cost of natural gas (NG) and the cost of emitting CO₂ into the atmosphere while holding the cost of coal at \$2/ GJ. In Figure 26, we assume that the captured CO₂ can be used for EOR, whereas in Figure 27, we assume that the captured CO₂ must be sequestered in a saline aquifer. For the EOR case, we found that if the price of natural gas goes above the line between the points (\$10/tCO₂, \$5.0/GJ) and (\$50/tCO₂, \$2.5/GJ), then the Adv IGCC & IGFC -CCS-EOR configurations have the lowest levelized cost of electricity. Note also that there is line at which a NGCC-CCS power plant has the lowest value of LCOE and there is also a vertical line around \$10/tCO₂ at which a PCC has the lowest value of LCOE. There is also a horizontal line just below \$2.5/GJ, which shows when the Adv. IGCC & IGFC-CCS configurations and NGCC-CCS configurations have the same LCOE. For saline sequestration (ca. Figure 27), the area in the graph in which NGCC has the lowest value of LCOE increases substantially. The results in Figure 26 are fairly similar to the results presented in Figure 3 of Fischbeck *et al.* [163], who present a case in which captured carbon dioxide is assumed to obtain a sale price of \$25/tCO₂. However, one major difference is that our 'Coal with CCS' case was an Adv. IGCC-CCS configuration rather than a PC-CCS configuration.

The economic analyses conducted here suggest that there might be scenarios in which Adv IGCC & IGFC–CCS power plant configurations are economically preferable; however, this requires either an increase in the price of natural gas or an increase in the price of CO_2 emissions. It should also be noted that this analysis held the price of capital, labor, and coal constant while varying the price of natural gas and the price of CO_2 emissions. The price of capital, labor, and coal is unlikely to remain constant with changing price of natural gas and CO_2 emission, so the conclusion we drawn from these figures should not be used as predictions for future outcomes. Instead, they should be used to determine which power plant configurations deserve further research and development. It should be noted that the advanced IGCC and IGFC configuration studied here still require significant levels of research ansd development before they are commercially-viable for large scale power plants. Specifically, this means scaling up H₂

and O_2 membrane technology, further testing operation of gas turbines on hydrogen, scaling up the size of the catalytic gasifier, proving the catalyst regeneration process, and scaling up the size and pressure of SOFCs.



Figure 26: The lowest cost of electricity between PCC, NGCC, NGCC-CCS-EOR, Adv. IGFC-CCS-EOR, and Adv. IGCC-CCS-EOR, as a function of the price of natural gas and CO₂ emissions, assuming an EOR sale price of \$15 / ton of CO₂, using cost estimates from Gerdes *et al.* [31, 32]. The price of coal was held constant at \$2/GJ in 2007USD.



Figure 27: The lowest cost of electricity between PCC, NGCC, NGCC-CCS-SalSeq, Adv. IGFC-CCS-SalSeq, and Adv. IGCC-CCS-SalSeq, as a function of the price of natural gas and CO₂ emissions, assuming a Saline Sequestration cost of \$5 / ton of CO₂, using cost estimates from Gerdes *et al.* [31, 32]. The price of coal was held constant at \$2/GJ in 2007USD.

5.5 Conclusions

We used capital and labor cost estimates from previous researchers in order to compare the IRR of these two advanced power plant designs with conventional and other advanced power plant designs. Using cost estimates from other studies and assuming recent fuel and electricity prices, a natural gas combined cycle (NGCC) power plant yielded the highest value of rate of return on investment (22%/yr).

However, our results suggest that, in the case of a CO_2 tax of \$25/t CO_2 , then three different configurations are equally viable economically (IRR = 8%/yr at \$50/MWh): a NGCC power plant without capture, an advanced IGCC-CCS-EOR power plant with H₂ and O₂ membranes, and an advanced IGFC-CCS-EOR power plant that integrates a catalytic coal gasifier with a pressurized SOFC.

This research suggests that there may be advanced coal-based power plants that can achieve values of IRR at or above 6%/yr at today's typical prices for baseload electricity generation of \$50/MWh; and therefore, research into advanced H₂ and O₂ separation membranes as well as pressurized SOFCs and catalytic gasifiers are of crucial importance to the development of low cost baseload electricity if the price of natural gas in the future goes above \$5/GJ and the price of CO₂ emissions goes above \$20/tCO₂. The calculations in this report suggest that there may be scenarios in which advanced IGCC and IGFC configuration are economically viable, meriting further research and development into these technologies.

Chapter 6 Exergy & economic analysis of biogas fueled SOFCs

6.1 Introduction

Renewable fuels that do not decrease crop land and that do not require large inputs of fossil fuels are one of many promising means of generating electricity and positive economic benefits without increasing the cost of food and without having a net effect on the concentration of carbon dioxide in the atmosphere. One such fuel that fits this description is municipal wastewater. In 2004, the United States generated over 120 billion liters/day of municipal wastewater [167], which amounts to approximately 100 gallons of wastewater per day per person. Typical values of waste water chemical oxygen demand (COD) in Europe and the US vary between 0.2 and 0.6 g/L [168]. Assuming an average COD of 0.5 g/L, the waste water in the US has a potential chemical enthalpy of about 14 GW_{th}. Assuming that the chemical enthalpy in wastewater can be converted into electricity at an efficiency of 50%, the wastewater produced in the US can generate on average roughly 7 GW of electricity. This is on the order of 1% of 490 GW of time-averaged electricity generation in the US in 2010 [169]. While this value is small compared to the total electricity generation in the US, this value should not be overlooked. In addition, the conversion of chemical enthalpy of wastewater into electricity represents a viable market

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for fuel cell systems in the near future because the scale of typical wastewater treatment plants corresponds closely with the size of today's large-scale fuel cell systems (100 kW to 1 MW).

Currently, most wastewater treatment plants in the US use aerobic bacteria to oxidize the COD in waste water as opposed to anaerobic digestion [170]. For example, of the roughly 130 waste water treatment plants in Massachusetts as of 2011, only 6 of them were using or were in the process of installing anaerobic digesters at the treatment facility [171]. In 2002, aerobic digesters consumed approximately 1.5% of the electricity generated in the US [172]. The pumps and air blowers required to operate aerobic digesters consume electricity, and in the aerobic digester, there is near complete exergy destruction of the original exergy in the wastewater because the chemical reactions are occurring near room temperature and pressure, and hence can't be used to generate useful work.

However, there are now a growing number of waste water treatment plants globally that use anaerobic digesters [173]. In addition, there are now a few cases in which the biogas from the waste water anaerobic digesters (AD) is sent directly to fuel cell systems. One example is the King County Carbonate Fuel Cell Demonstration Project [174], which in 2004-2005 integrated an anaerobic digester with a 1-MW molten carbonate fuel cell produced by Fuel Cell Energy (AD-MCFC.) Another example is the recent start-up of a 1.4 MW molten carbonate fuel cell at a waste water treatment facility in San Jose [175] and the planned 0.2 MW molten carbonate fuel cell at a waste water treatment facility in Wyoming [176]. There have been a number of previous numerical simulations and economic studies on integrating molten carbonate fuel cells with anaerobic digesters [177-179], as well as simulations on integrating solid oxide fuel cells with anaerobic digesters [137, 180, 181].

While molten carbonate fuel cell systems (a) can use biogas as fuel, (b) can generate electricity at a relatively high system efficiency and (c) are commercially available technology, we decided here to model a solid oxide fuel cell rather than a molten carbonate fuel cell because: (a) the all-ceramic SOFC materials are likely in the long run to be able to achieve both higher voltages at a given current density and lower capital costs per power generated than MCFC technology [182]; (b) the Department of Energy (DOE) via the solid state energy conversion alliance (SECA) publishes cost estimates and cost targets for SOFC stack technologies; and (c) Rolls Royce Fuel Cell Systems has made their V-*i* curves publically-available for their pressurized fuel cell systems [117]. The goal of this paper is to determine the economic feasibility of a biogas fed solid oxide fuel cell system so that waste water treatment plants can become net generators of electricity rather than consumers of electricity. In order to reduce normalized upfront capital costs (\$/kW) associated with anaerobic digester technology, it will be crucial

to achieve power plant system efficiencies above 50%. The most studied means of achieving the high system efficiencies required to keep down normalized upfront AD capital costs is to pressurize the fuel cell stacks and generate net electricity from the combined compressor-expander [183-189]. Here, we show here that AD-SOFC systems can convert WWT plants in net generators of electricity rather than net consumers of electricity while generating positives rates of return on investment at today's price of commercial electricity if DOE/SECA cost targets can be reached.

6.2 Process flow Diagram: AD – Hybrid SOFC

Figure 28 shows a process flow diagram of the AD - hybrid SOFC power plant system. The main components of this system are: (a) the anaerobic digester, (b) the SOFC, (c) a gas turbine (i.e. compressor, combustor, & expander), (d) heat exchangers, and (e) balance of plant, i.e. filters, pumps, fuel compressor, etc. The system was modeled using HSC Chemistry 6.0 (Outotec, Espoo, Finland), and the model was exported to Excel (Microsoft, Seattle, WA) in order to perform an economic optimization using a Visual Basic macro. Before going into detailed discussions of each of the main components, our goal here is to discuss the overall process flow diagram. New pieces of equipment are shown in gray, and assumed existing equipment is shown in gold. We used a hydrocyclone to generate a high COD waste stream (12 g/L) to send to a new AD and a low COD waste water stream (<0.5 g/L) to send to existing aerobic digesters at the WWT plant. The un-reacted solid and liquid biomass from the AD is sent to the existing aerobic digester. The biogas from the AD is compressed, goes through a heat exchanger, and then enters the H₂S polishing and siloxane removal reactor. Bulk H₂S capture is accomplished in the AD through the use of sacrificial iron oxides. The H₂S polishing step is done using ZnO and a separate reactor that regenerates the ZnO (not shown.) This high temperature reactor catalyzes the breakdown of siloxanes into silicates, effectively removing siloxanes before the SOFC. The gases exiting the anode and cathode of the SOFC are combusted and sent to a gas turbine before the exhaust gas is used to heat exchange with the incoming fuel and air, as well as used to transfer thermal energy to the AD to maintain the temperature of the AD at 55°C. We now discuss the details of each of the main components of the AD-SOFC system.



Figure 28: Process Flow Diagram of the anaerobic digester, pressurized SOFC power plant. Gray boxes indicate new equipment for the WWT plant and the dashed box indicates existing equipment at the WWT plant.

6.2.1 Anaerobic digester modeling

Inside of an anaerobic digester, bacteria convert organic solid materials into various organic gaseous and liquid products, including methane, carbon dioxide and acetate [190]. We modeled a thermophilic anaerobic digester based mainly off of an existing waste water treatment plant similar to the anaerobic digester examined by Derelli *et al.* [191]. Even though anaerobic digestion is an exothermic process (i.e. glucose to a 50%/50% CH₄/CO₂ biogas has a Δ H = -147 kJ/mol and a Δ G = -446 kJ/mol at 55°C), we assume that the reactor is maintained at 55°C through the use of heat supplied by the exhaust air from the power generation equipment.

To model the thermophilic anaerobic digester, we used experimental results from operating anaerobic digesters by previous research groups. For example, De la Rubia *et al.* [192] operated an anaerobic

digester at 55°C with a COD of 35 g/L and a normalized loading rate of 2.6 kg VS/m³-day. After a retention time of 15 days, they measured 42% removal of the COD. An EPA report by Gray *et al.* [193] measured between 40% and 60% removal of COD after 15 days in a thermophilic anaerobic digester when the normalized loading rate was between 2-4 kg VS/m³-day of municipal wastewater. In lab-scale experiments [194], it was determined that the reaction of COD into biogas was first order for values of COD in the digester less than 1 g/L, but for values of COD above approximately 10 g/L, the reaction order was zeroth-order. Since we are assuming that the COD of the wastewater into the treatment facility is initially 0.5 g/L, one would expect that there are diminishing returns for concentrating the waste water to a value much higher than 10 g/L.

In order to keep anaerobic digester costs reasonably low, we have placed a hydrocyclone before the anaerobic digester in order to increase the COD of the waste water from the national average COD of roughly 0.5 g/L to a value of 12 g/L. The high COD stream from the hydrocyclone goes to the anaerobic digester and the low COD stream from the hydrocyclone goes to the existing aerobic digesters. Based on previous studies of anaerobic digestion at wastewater treatment plants listed above and scaling their results to different values of COD, we present in Table 39 the assumed values for key aspects of the anaerobic digester. Using the assumptions in Table 39, the following values can be calculated: (1) the total solids flow rate into the reactor is 12,300 kg / day; (2) the normalized solid flow rate is 0.85 kg VS / m^3 day; (3) the liquid flow rate before the hydrocyclone is 25,000 m^3 /day, which corresponds to roughly 6.6 million gallons per day (mgd) of wastewater with a COD 0.5 g/L. This value is in line with the typical flow rate entering a municipal waste water treatment facility (1-10 mgd) [195]. The facility modeled here would treat ~0.02% of the total wastewater processed in the US.

Next, we performed sizing analysis for the anaerobic digester. In order to first determine the digester volume, the solids flowrate was multiplied by the retention time and then divided by the chemical oxygen demand (COD), a measure of the organics concentration. The volume was calculated to be 14,200 m³. Greer [196] calculated that a Michigan-based agricultural digester with a volume of 2100 m³ would cost \$350,000. To determine the cost of the 14,200 m³ AD reactor here, we assumed that capital costs would scale with the volume to power of 0.75. Hence, the total cost of our anaerobic digester was \$1.5 million (US\$ 2010), with a likely uncertainty of \pm 30%. For comparison, we also checked this value with cost estimates for carbon steel mixing tanks in Perry's Chemical Engineering Handbook 8th Ed. (Fig. 9-4) [93], and estimated a value of \$1.8 Million (US\$ 2010) after adjusting for inflation. The AD was the largest cost component in the entire system. To put this AD capital cost in

perspective, if the 2 mol/s of CH₄ being generated from this AD were converted into electricity with 25% efficiency, the normalized capital cost of just the AD equipment would be approximately \$4000/kW. For this reason, it is crucial to operate the entire system at fairly high values of system efficiency in order to keep down the normalized capital cost associated with the AD.

Variable	Value		
Temperature	55 °C		
COD value entering AD	12 kg/m ³		
Liquid flow rate into the	1,030 m ³ /day		
reactor			
COD removal	85%		
Retention time inside AD	14 days		
Outlet gas pressure	0.1 MPa		
Total Reactor Volume	$14,200 \text{ m}^3$		
Total Cost (US\$ 2010)	\$1.5 million		

]	Fable	39:	Process	and	economic	assumption	ns for	the	anaerobic	digester	at a	waste	water	treatm	ent
p	olant	after	using a	ı hyd	rocyclone	to increase	the C	OD							

6.2.2 Solid oxide fuel cell modeling

There have been a number of research groups that have already obtained successful experimental results using the internal reforming of biogas to power a SOFC [137-141, 197-202]. For example, Shiratori *et al.* [140] showed experimental operation of a SOFC for 50 h with direct biogas using a Ni-ScSZ cermet as the anode material without external reforming of the biogas. The gas composition sent to the SOFC was approximately 62% CH₄, 36% CO₂, 2% H₂O from an anaerobic digester operating at 35–38°C. After 50 hours of operation, they did not see any carbon formation on the anode. They did measure a roughly 100 mV drop in operating voltage when 1 ppm of H₂S was added into the biogas stream. The cell voltage gained back the 100 mV drop in voltage after the 1 ppm level of H₂S was removed. In a subsequent paper, Shiratori *et al.*[139] operated the SOFC at 800°C, and they measured continuous degradation in operating voltage with a 1 pmm concentration of H₂S, which eventually

caused fatal shutdown of the SOFC. Shiratori *et al.*[139] also saw significant deposit of carbon when they ran at 800°C for over 700 hours of operation. Interestingly, there was no carbon deposit when they operated using simulated biogas. This suggests that carbon deposition is more complicated than simply knowing the C:H:O ratio in the anode. Shiratori *et al.* [140] have operated a SOFC for 50 h directly on biogas while using a Ni-ScSZ cermet as their anode material. On the other hand, Staniforth and Kendall [202] determined that there would be major issues with carbon deposition unless small amounts of air were added to the fuel stream before entering the anode inlet of the SOFC.

While it is the case that anodes composed of pure Ni-YSZ are not tolerant to high levels of H_2S or to hydrocarbons, Yang *et al.* [142] have shown experimentally that Ni-YSZ anodes doped with barium and cerium are more tolerant to both hydrogen sulfide and propane. In addition, Lanzini *et al.* [138] measured experimental V-*i* curves of SOFCs operating on biogas while also generating a fuel cell model to explain the experimental results. Laycock *et al.* [141] studied the effect of ceria doping on SOFC performance when operating on biogas. They found that there appear to be trade-offs between increased sulfur tolerance and increased carbon deposition when using ceria doped Ni-YSZ.

The conclusions we draw from prior research are the following: (a) the concentration of H_2S must be less than 1 ppm if pure Ni-YSZ is the anode material, and (b) there either must be a significant amount of anode gas recycle or must be a significant amount of carbon dioxide and water vapor in the biogas in order to reform methane and to minimize carbon deposition. Even though future SOFC anode materials may be sulfur tolerant, in this study, we do not assume that the Ni-YSZ anode is doped with materials to improve the sulfur tolerance. Therefore, in the next section, we discuss cost effective means of reducing the H_2S concentration to less than 1 ppm.

Using the constraints listed above, we modeled the SOFC using publically-available data from Rolls Royce Fuel Cell Systems [117], who have presented V-*i* curves for their SOFC stack at various SOFC temperatures and pressures. We used the same V-I curves as in previous chapters for pressurized SOFC systems. In Figure 29, we present voltage vs. current density and power density vs. current density curves for a case when the fuel cell is operated at a pressure of 300 kPa, and a temperature of 850°C.



Figure 29: Voltage and power density versus current density at a pressure of 300 kPa, and a temperature of 850°C, extrapolated from publically-available data from Rolls Royce Fuel Cell Systems [117].

Due to the sheer number of possible free variables in this hybrid SOFC-gas turbine system, we decided to fix a few of the variables and to place some constraints on the system. For example, we maintained a fuel inlet temperature at 800°C; we maintained an air inlet temperature at 750°C; we limited the temperature difference between the air inlet and air outlet to be less than 130°C; and we assumed that the composition of carbon dioxide plus water vapor in the biogas was greater than the composition of methane in the biogas, i.e. 45% CH₄, 40% CO₂ 15%H₂O, so that the methane in the biogas could be reformed by H₂O and CO₂ at the inlet of the anode. It should be noted that the 15% H₂O in the biogas at 55°C means that the relative humidity is 100%.

In addition to these thermodynamic assumptions and constraints, we made assumptions on the mass production costs of SOFC stacks and systems using estimates from the U.S. Department of Energy (DOE) and the Solid state Energy Conversion Alliance (SECA). From Gerdes *et al.* [31] and the SECA goal of system costs at \$400/kW, we estimated that the SOFC stack cost would be \$1700 per m² of active area (\pm 40%), that the SOFC enclosure would be \$80·(p[atm])^{0.33} per kW generated in the SOFC (\pm 40%), that the SOFC stack replacement would be \$175 per kW generated in the SOFC (\pm 40%); and that the DC/AC inverter cost would be \$70 per kW generated in the SOFC. Here, we have chosen to break the SOFC costs down into their main components, rather than to leave the costs in "per kW" so

that we could correctly account for the fact that costs should scale with the required active area. Li *et al.* [29] did a cost estimate of an integrated gasification fuel cell system and assumed that system costs were \$400/kW stack capital cost. Though, an approach similar to our chosen cost estimating approach was done by Piroonlerkgul *et al.* [118], who assumed that stack costs would increase linearly with the active area. In their 2009 report, they used a value of \$1442 per m² of active area. Our use of \$1700 per m² of active area reflects the increase in rare earth metals since 2009. We have given the stack replacement costs in "per kW" because we assume that degradation of the fuel cell, i.e. the increase in the ASR with time, depends on the total power produced from the fuel cell. This is the reason that the stack replacement costs are not given in units of "per m² of active area" as was the SOFC stack cost. In the next section, we discuss the means by which pollutants in the biogas are removed before reaching the anode of the SOFC.

6.2.3 Sulfur and siloxane capture

There are a few species in the biogas that can do significant damage to the fuel cell anode. Two of the main species are sulfides and siloxanes. Here, we discuss the chosen system for removing sulfide species (such as hydrogen sulfide and carbonyl sulfide) and siloxanes. In Appendix A, we discuss the reasoning that led to our chosen means of capturing these species, which if left un-captured, would quickly degrade the power density of the fuel cell system. In Appendix A, we discuss other options available for sulfur and siloxane capture, as well as the relative advantages and disadvantages of each option. The reason we do this is that the capture of sulfide and siloxane species can be a major cost if they are removed using conventional physical adsorption processes that operate at below room temperature. We first discuss capture of H_2S and COS before discussing the capture of siloxanes.

The concentration of hydrogen sulfide in waste water biogas can be in the range of 0 to 6000 ppm depending on the feedstock [203, 204]. Here, we assume that the H₂S+COS composition would be 1000 ppm without capture techniques, similar to the average value of roughly 800 ppm reported by Trendewicz *et al.* [180] for an anaerobic waste water treatment facility in Denver. We wanted to make sure that the chosen sulfur removal process would be able to capture both H₂S and COS because both sulfide species can turn electro-catalytic nickel metal into non-catalytic nickel sulfide [205]. As elaborated upon in Appendix A, we decided to accomplish bulk removal of sulfide species inside of the

anaerobic digester through the addition of iron (III) oxides. The reactions for capturing sulfur species inside of the AD using iron (III) oxide are listed below, along with the change in Gibbs free energy. The values of Gibbs free energy were obtained using HSC Chemistry 6.0 (Outotec, Espoo, Finland).

$$Fe_2O_3 + 3H_2S(g) = Fe_2S_3 + 3H_2O(l)$$
 $\Delta G(55^{\circ}C) = -142 \text{ kJ/mol}$ (30)

$$Fe_2O_3 + 3COS(g) = Fe_2S_3 + 3CO_2(g)$$
 $\Delta G(55^{\circ}C) = -226 \text{ kJ/mol}$ (31)

One advantage of adding iron oxide directly in the anaerobic digester, in addition to its ability to capture sulfur species, is that this process can potentially increase the kinetics of methanogenesis [206] without significantly lowering or raising the pH of the AD. It should be noted that adding alkali and alkali earth capture agents into the anaerobic digester will alter the pH, which would likely have a detrimental effect on the kinetics of the anaerobic digester. For example, Liu *et al.* [207] determined that the optimal pH for either mesophilic or thermophilic digestion is roughly pH 7.2. They determined that an increase in the pH from 7.2 to 8.0 would cause a threefold decrease in the cumulative methane production after a fixed amount of time, and that a decrease in pH to 6.0 would cause a roughly twofold decrease in cumulative production.

As recently found by Kato *et al.* [206], the addition of electrically conductive forms of iron oxide can significantly increase the rate of methanogenesis. Hematite and magnetite both increased the kinetic rates for methanogenesis by *Geobacter* spp compared with when these conductive forms of iron oxide were swapped with an insulator, ferrihydrite. Therefore, the addition of electrically conductive forms of iron oxide appears to be a promising means of increasing the kinetics of methane formation while also capturing sulfide species. However, since the experiments were conducted using a different feedstock, we did not account for this increased rate of methanogenosis even though, in our model, we added iron oxide for bulk capture of sulfur species from 1000 ppm down to 100 ppm. In the economic analysis, we include a cost for adding sacrificial hematite at a cost of \$100 / ton. Using estimates from a report by Washington State Department of Ecology [208], we assume that 1 kg of iron oxide can capture 0.2 kg of H₂S. This means that 1 kg of iron oxide is required for every 50 kg of biomass entering the AD. Therefore, the iron addition costs are roughly \$0.50 / ton of biomass entering the AD.

Since we need to remove sulfur species to below 1 ppm, we've added a sulfur polishing step just before the SOFC. Zinc oxide is a well known capture agent for hydrogen sulfide and carbonyl sulfide, and can achieve combined sulfur concentrations below 1 ppm [104-109]. The reactions and the change

in Gibbs free energy are listed below. In addition, we list the Gibbs free energy for the CO₂ capture reaction and the hydrogen oxidation reaction to show that the zinc oxide will not capture CO₂ at 600°C and that the zinc oxide will not convert to molten, metallic zinc under these reducing conditions. At temperatures above 300°C, zinc oxide should be able to capture phosphine, PH₃, which is another known pollutant for SOFC anodes [209] and which is found in biogas on the order of 0-200 ppm [210]. While this zinc oxide bed was chosen for its multi-functional purpose, we did not include phosphine in our model of the biogas-SOFC process because it is found in lower quantities than sulfides in biogas, but reacts similarly to sulfides in zinc oxide beds. One reason that phosphine is in much lower quantities in biogas than sulfide, even if sulfur and phosphorous are in equal composition in biomass, is that hydrogen phosphate anions $(H_2PO_4^{-2})$ are significantly more stable than sulfate (SO_4^{-2}) anions at the pH and reduced oxygen potential (ORP) of anaerobic digesters. The relevant reactions in the ZnO capture and desorption beds are listed below.

$$ZnO + COS(g) = ZnS + CO_2(g) \qquad \qquad \Delta G(600^{\circ}C) = -105 \text{ kJ/mol}$$
(32)

$$ZnO + H_2S(g) = ZnS + H_2O(g)$$
 $\Delta G(600^{\circ}C) = -73 \text{ kJ/mol}$ (33)

$$ZnO + 2 PH_3(g) = ZnP_2 + 2 H_2(g) + H_2O(g) \qquad \Delta G(600^{\circ}C) = -28 \text{ kJ/mol}$$
(34)

$$ZnO + CO_2(g) = ZnCO_3 \qquad \qquad \Delta G(600^{\circ}C) = +79 \text{ kJ/mol} \qquad (35)$$

$$ZnO + H_2(g) = Zn + H_2O(g)$$
 $\Delta G(600^{\circ}C) = +62 \text{ kJ/mol}$ (36)

$$ZnS + 1.5 O_2(g) = ZnO + SO_2(g)$$
 $\Delta G(750^{\circ}C) = -365 \text{ kJ/mol}$ (37)

As seen in Eq (32), the ZnS is regenerated by oxidizing zinc and generating gaseous sulfite. Multiple groups have demonstrated regeneration of ZnO-based capture agents without significant formation of zinc sulfate [109-113]. For example, Sanchez-Herva *et al.* [109] showed using the Z-Sorb III sorbet that, even after 9 cycles of sulfidation and regeneration, there was very little sulfate formation. One key here is to send in just enough oxygen to form S in the +4 (IV) state and not enough to form S in the +6 (VI) state. The selective capture of sulfides and the ability to regenerate make ZnO an ideal material for capturing H₂S from biogas. In theory, this process could be used to capture all of the sulfur species in the biogas; however, we chose to use this only for polishing and to use iron oxides for H₂S capture inside of the AD because iron addition to the AD is likely to improve the kinetics of methangenosis in such a way that the iron oxide addition will likely pay for its reoccurring costs by reducing the size of the AD, for a given required production rate of biogas. In our model, the acid gases from the regenerator

are sent to the aerobic digester so that the sulfite and sulfate are not released to the atmosphere. The pH of the aerobic digester is maintained using calcium carbonate, so that the ultimate fate of sulfur species in this process is either calcium sulfate or iron sulfide.

In addition to removing sulfur species, the zinc oxide bed also provides a catalyst bed for decomposing siloxanes before they can reach the anode of the SOFC. Siloxanes are silicon-containing ring-structures that are slightly volatile near room temperatures. The composition of siloxanes in biogas is typically on the order of 0-140 mg/m³ [211-213], of which the main siloxanes are labeled L2, D4 and D5. Known methods of removal are: absorption into polyethylene glycol (Selexol), adsorption on activated carbon at low temperatures [214-216], absorption into concentrated sulfuric acid (>50%) [211], and/or thermal decomposition on acidic oxides at elevated temperatures [211, 217-219]. Siloxanes are known to damage the anodes of SOFCs [137] as well as known to damage piston and turbine engines because their thermal decomposition leaves silica on the walls of the equipment. Like sulfides, the concentration of siloxanes should be reduced to less than 1 ppm. However, it should be noted that siloxanes are not a major concern for the process designed here because the sulfur capture process (zinc oxides on alumina support particles) was chosen specifically for its multi-purpose functionality. The acidic alumina sites on the support will act as catalyst sites for thermal decomposition of the siloxanes before they reach the anode of the SOFC.

To estimate the capital cost of this zinc oxide two-fluidized-bed reactor, we relied on a cost estimate from Nexant (San Francisco, CA), who estimated a cost of \$42 million (2001 US\$) for a system that would capture H₂S and COS in the syngas at a 500 MW IGCC power plant [220]. After using a scaling exponent of 0.8 and converting this to our pressure, size, flow rate, sulfur content, and 2010 US\$, we obtained a cost estimate of \$300,000 (\pm 30%) for the cost of the sulfur capture (and siloxane decomposition) reactor, which was one fifth of the cost of the AD. If all of the sulfur capture was done outside of the AD, then the cost of the sulfur removal equipment would be nearly equal to the cost of the AD, which is already quite expensive. This was one of the main reasons that we decided to do the bulk of the H₂S capture inside of the AD.

6.2.4 Balance of plant

Here, we discuss the assumptions for the equipment that make up the balance of plant. For all compressors and expanders, we have assumed an isentropic efficiency of 75% and we have assumed that

the cost of all compressors and expanders is equal to \$200 (Power[kW]), which we have estimated from Silla et al. [119]. We assumed that the maximum firing temperature of the combustor was 1600 K, based off of the maximum firing temperature of a GE 6FA gas turbine. For heat exchanger costs, we assume a cost of \$1 / cm² of required cross section, as estimated by Silla et al. [119] at the low end of heat exchanger sizes. It should be noted that heat exchanger costs were insignificant compared with the cost of the AD in this AD-SOFC system. All heat exchangers were counter-flow, and we required that the temperature difference from the hot and cold side of the heat exchanger at any point along the length never drop below 30 K, i.e. a minimum pinch point of 30 K. The hydrocyclone was estimated to be \$300,000 based off of commercially available units that could generate 1,030 m³/day of waste water with a COD of 12 kg/m³ from an initial COD of 0.5 kg/m³. The hydrocylcone consumes 30 kW of electricity, which is roughly 1.5% of the exergy in the biomass converted in the AD. We have included a pressure drop of 20 kPa through the fuel side in order to model pressure drop through the heat exchangers, the fuel cell, and the zinc oxide fluidized-bed. We have included a pressure drop through the air side of $20 \cdot \lambda_{air}$ kPa, where λ_{air} is the total air stoichiometric ratio. λ_{air} is the ratio of the oxygen in the inlet air divided by the sum of the oxygen consumed in the SOFC and the oxygen consumed in the combustor. We allowed this total air stoichiometric ratio to vary in our economic model, but we kept the size of all equipment the same as we varied the air stoichiometric ratio, which is why we modeled the pressure drop to be $20 \cdot \lambda_{air}$ kPa.

6.3 Exergy analysis

Here, we present an exergy analysis of the combined AD-SOFC system. We define the exergy efficiency to be equal to the net electrical work generated in the plant divided by the difference between the exergy in biomass entering the AD and the exergy in the biomass leaving the AD. This definition is used to compare with other biogas-fed power systems, but it should be noted that the choice of definition of exergy efficiency has no effect on our economic calculations. In the definition below, we assume that the exhaust has equilibrated with the environment before leaving the system.

$$\eta_{\text{exergy}} = \frac{\sum \dot{W}_{electric}}{(\dot{n}\cdot \hat{e})_{AD-inlet} - (\dot{n}\cdot \hat{e})_{AD-outlet-liquid}} = 1 - \frac{\sum T_0 \cdot \sigma_{irr}}{(\dot{n}\cdot \hat{e})_{AD-inlet} - (\dot{n}\cdot \hat{e})_{AD-outlet-liquid}}$$
(38)

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In Table 40, we present the power generated/consumed as well as the exergy destruction in each of the main components of the system. In our system model, there were four free variables (pressure, current density, air stoichiometric ratios and fuel utilitization) and a number of constraints (maximum fuel utilization of 80%, minimum air stoichiometric ratio of 1.5, minimum pinch point temperature of 30 K, max firing temperature of 1600 K, anode inlet temperature of 1073 K, cathode inlet temperature of 1023 K, and maximum temperature at the exit of the cathode of 1153 K.) This means that the exergy destruction in each of the main components of the system will depend on the choice of the four independent variables. In Table 40, the values of power generation/consumption and exergy destruction are given at the value of pressure, current density, air that minimized the normalized capital costs. As will be shown in the next section, we found that the optimal values were at a pressure of 250 kPa, a current density of 0.7 A/cm², an air stoichiometric ratio of 1.5, and a fuel utilization of 80%.

Table 40: Normalized power and normalized exergy destruction for the major processes in the AD-SOFC system. These results were generated at the case that minimized normalized capital costs of the system. The conditions were the following: fuel utilization in SOFC of 80%, total air stoichiometric ratio of 1.5, SOFC pressure of 250 kPa, current density of 0.7 A/cm², and SOFC temperature of 877°C. The normalized capital cost under these conditions was approximately \$3600/kW.

Process Step	Power /	Exergy Destruction		
	Inlet Exergy	/ Inlet Exergy		
Digester + Exhaust Air	-1.5%	22.2%		
Fuel Compressor	-0.9%	0.1%		
Air Compressor	-7.1%	1.1%		
Combustor		6.3%		
Exhaust Turbine	+15.3%	1.2%		
HX#1&HX#2		4.0%		
SOFC	52.3%	7.0%		
SUM	58.1%	41.9%		

As seen in Table 40, the exergy efficiency of the power plant under these conditions was 58%. This means that, of the exergy in the waste that entered the AD and was converted to biogas, 58% of the exergy leaves the plant in the form of electricity and 42% of the exergy was destroyed in irreversible processes, such as electro-chemical reactions, heat transfer, and momentum transfer. The largest source of exergy destruction was the anaerobic digester (22.2%). This value was a combination of 19.6% associated with the methangenosis reactions and 1.6% associated with exergy lost due to heat transfer to the environment from the exhaust air used to keep the AD at a temperature of 55°C. The second largest source of exergy destruction was the SOFC; though, the SOFC was the largest source of power generation. The third largest source of exergy destruction at this set of independent variables was the combustor. At fuel utilization values near 60% (not shown), the combustor can become the largest source of exergy destruction.

In Figure 30, we present the exergy efficiency of the integrated AD-SOFC power plant as a function of the current density at a range of different values of the other free variables: pressure, fuel utilization, and air stoichiometric ratio. At a given value of current density, the highest value of exergy efficiency occurred at a value of fuel utilization of 80%. The exergy efficiency monotonically decreases with increasing current density for any choice of the other three variables. As listed in Eq. (15), the exergy efficiency is defined as the electricity output divided by the exergy in the biomass that gets converted into biogas. In other words, this value of exergy efficiency does not account for the biomass that passes through AD unconverted and is sent to the aerobic digester.



Figure 30: Exergy efficiency of the overall AD-SOFC power plant as a function of current density for a range of different values of pressure, fuel utilization, and air stoichiometric ratio.

It should be noted that the choice of boundary for defining the exergy efficiency can be arbitrary, and this is one of the reasons that we did not optimize our power plant system to maximize the exergy efficiency in converting waste into electricity. Instead, we optimized our power plant system to minimize the normalized capital costs, which would also yield a minimized value of the levelized cost of electricity assuming zero fuel costs, as will be discussed next.

6.4 Economic analysis

6.4.1 Optimization to minimize normalized capital costs

In addition to conducting an exergy analysis, we conducted a Feasibility Study, which is a Class 4 Capital Cost Estimate according to the definition from the association for the advancement of cost engineering international (AACE). A Class 4 Capital Cost Estimate typically occurs when: (a) project definition is 1%-15%; (b) there is a process flow diagram and equipment lists; and (c) the expected accuracy in the cost estimate is -15% to -30% on the low side and +20% to +50% on the high side. This means that there will be significant uncertainty in the actual capital cost of the configurations analyzed in this study.

We used cost estimates from previous researchers and/or from chemical process engineering textbooks to estimate the cost of equipment as a function of the size of the equipment. This input is required in order to estimate the capital cost of the plant as a function of the four main independent variables: SOFC current density, fuel utilization in the SOFC, SOFC pressure, and the overall plant air stoichiometric ratio. Note that the first two variables determine the size of the SOFC and the last two variables determine the sizing and number of stages for the air compressor and exhaust expander. In Table 41, we summarize the cost assumptions in our full thermo-economic model, some of which have been listed in earlier sections. Note that all values listed below are in units of \$ = 2010 USD.

Table 41: Summary of AD-SOFC cost estimates

Equipment	Capital Cost Estimation	Uncertainty	Reference
Compressor or	\$200·(Power[kW])	$\pm 20\%$	[119]
Expander			
Heat Exchanger	\$1 per cm ² of cross sectional area required	± 40%	[119]
Hydrocyclone	\$300,000	± 30%	Commercially available
Anaerobic Digester	\$1,50,000 for three reactors	$\pm 30\%$	[196]
SOFC stack cost	\$1700 per m ² of active area	± 40%	Extrapolated from [31]
SOFC enclosure	\$80·(p[atm]) ^{0.33}	± 40%	Extrapolated from [31]
SOFC Stack	\$175 per kW generated in the	$\pm 40\%$	Estimated from
Replacement	SOFC at years 5, 10, and 15		[31]
DC/AC converter	\$70 per kW generated in the SOFC	± 20%	Estimated from [31]
Sulfur Polishing &	\$300,000	± 30%	Estimated from
Siloxane Removal			[221]
Lifetime	1 yr construction,		
	20 yrs of operation		
Capacity factor	80% of design power on average		
Engineering design,	50% of the sum of equipment		
Piping, Construction,	costs		
& Contingency (EPCC)			

In addition to the cost assumptions discussed in previous sections, we assumed that the power plant could be constructed in one year and operate with an capacity factor of 80% (i.e. 80% of design power on average) for a total of 20 years. Given that the stack replacement time was assumed to be 5 years, this means that in years 5, 10 & 15 there would be a cost of \$175 per each kW of power generated in the SOFC. The total capital costs were calculated to be the 1.5 times the total equipment costs. This factor of 1.5 assumes that engineering, piping, construction and contingency (EPCC) is equal to 50% of the sum of equipment costs. We are assuming that this AD-SOFC will be built at an existing WWT that already has basic utility connection. As well, we assumed that the land and the existing aerobic digester has already been purchased. To determine the normalized capital cost of the system, we divided the total capital costs (including the 50% EPCC factor) by the total power generated by the system.

As mentioned previously, in our system model, there were four independent variables that can be varied in order to minimize the normalized capital costs. In Figure 31, we graph the normalized capital

costs in [2010 US\$ per kW] as a function of current density at the same set of conditions as in Figure 30. A Visual Basic macro was created to calculate the normalized capital cost at a range of different input variables. The range consisted of the following: pressures from 150 kPa to 600 kPa in increments of 50 kPa; fuel utilization from 60% to 80% in increments of 5%; total air stoichiometric ratio from 1.5 to 3.0 in increments of 0.25; and current density from 0.1 A/cm² to 1.0 A/cm² in increments of 0.1 A/cm². Though in Figure 31, we only present a select few of the data points around the minimum value of \$3600 for the normalized capital cost in order to focus on the region near the extrema. The lowest values of normalized capital cost were achieved when the fuel utilization reached its upper limit of 80%, which was a constraint we placed on the system because of experimental evidence showing increased anode degradation with increased values of fuel utilization [222]. We found that the lowest value of normalized capital cost occurred at a fuel utilization of 80%, a total air stoichiometric ratio of 1.5, a SOFC pressure of 250 kPa, and a current density of 0.7 A/cm^2 .

As was found in Figure 30, the highest values of exergy efficiency also occurred at these values of fuel utilization, total air stoichiometric ratio, and pressure. The exergy efficiency was an extrema at the lowest value of current density for any give choice of fuel utilization, total air stoichiometric ratio, and pressure; however, the normalized capital cost was typically an extrema at an intermediate value of current density around 0.7 A/cm². At values significantly below 0.7 A/cm², the normalized capital costs are relatively large because the SOFC capital costs increase with increasing active area. At values significantly above 0.7 A/cm², the normalized capital costs are relatively large because the exergy efficiency is relatively low and hence the normalized cost of the non-SOFC equipment starts increasing.

Given the large uncertainty (around \pm 30%) in many of components, there is a large range of values of pressure, current density, fuel utilization and air stoichiometric ratio that could yield lowest value of normalized capital cost depending on the relative uncertainty in the cost of the SOFC equipment compared with the AD equipment. So, in a sense, there is no true optimal choice of free variable in the AD-SOFC system because there are many choices of the four independent parameter that yield values of normalized cost in the range of \$3600/kW to \$4000/kW, which is well within the range of uncertainty in capital cost of \pm 30%.



Figure 31: Normalized capital cost of the overall AD-SOFC power plant as a function of current density for a range of different values of pressure, fuel utilization, and air stoichiometric ratio. The curves do not cover the full range of current density because of the various system constraints, such as heat exchanger inlet and outlet temperatures. Dollar values are in 2010 US\$.

We also analyze in Figure 32 the case in which the SOFC stack and stack replacement costs are double the assumptions above. Here, we assume that the stack costs are \$3400/m² and the stack replacement costs are \$350/kW. In this case, the optimal current densities shift higher, as would be expected if the stack costs increase. However, the overall effect of a stack cost doubling did not have a significant effect of the normalized capital cost. The minimum value increased from \$3600/kW to \$4000/kW.



Figure 32: Normalized capital cost of the overall AD-SOFC power plant as a function of current density for a range of different values of pressure, fuel utilization, and air stoichiometric ratio when the SOFC stack and stack replacement cost assumptions are doubled. Dollar values are in 2010 US\$.

6.4.2 IRR Analysis

Because a normalized capital cost (\$/kW) does not include information on maintenance costs, we have conducted a rate of return on investment analysis of this power plant configuration assuming that the power plant can obtain \$80/MWh for the electricity it generates during the 20 year lifetime assuming that its capacity factor was on average 80% of its rated power and that the variable operating cost was \$20/MWh regardless of the choice of current density, pressure, fuel utilization and air stoichiometric ratio. The internal rate of return on investment (IRR) is calculated by finding the interest rate, *i* that makes the net present value (NPV) of the cash-flow time-series in years 0 through 20 equal to zero.

$$NPV = 0 = \sum_{t=0}^{N} \frac{C_t}{(1+i)^t}$$
(39)

where C_t is the cash-flow time-series (net income or loss in year *t*), and *N* is the total lifetime of the power plant [128]. The IRR is the average rate of return on investment that an equity investor would obtain if dividends are re-invested into an exactly similar projects. We conducted an IRR analysis so that we could compare the relative economic viability of an AD-SOFC with systems in which the AD is integrated with a piston engine or a micro turbine.



Figure 33: IRR of the overall AD-SOFC power plant project as a function of current density for a range of different values of pressure, fuel utilization, and air stoichiometric ratio. The curves do not cover the full range of current density because of the various system constraints. Overall plant assumptions were: \$80/MWh electricity sale price, 1 yr construction, 20 yr operating lifetime, SOFC stack replacement at years 5, 10 & 15, capacity factor of 80%, and maintenance of \$20/MWh independent of the normalized capital cost. Dollar values are in 2010 US\$.

While the choice of electricity price will depend greatly on the location of such a power plant, in Figure 33 we chose a value of \$80/MWh, which was in between the average commercial price of electricity in 2010 (\$102/MWh) and the average industrial price of electricity in 2010 (\$68/MWh), as determined by the US Energy Information Administration [223]. We used a larger value of electricity sale price than in previous chapters because it was assumed that this electricity would offset electricity consumed at the wastewater treatment plant, which would likely be higher than the price it could receive if it tried to sell the electricity to the power grid. Given the assumptions made above, the AD-SOFC
system could potentially yield a pre-tax, inflation-adjusted IRR of $9\%/yr \pm 4\%/yr$. Here, the uncertainty is given only for the uncertainty in capital costs, not for any uncertainty in electricity prices, maintenance prices, lifetime or capacity factor.

If the SOFC stack and stack replacement costs were both doubled, then the normalized capital cost would increase to \$4000/kW and the IRR would decrease to 7%/yr. If the SOFC stack and stack replacement costs were both quadrupled, then the normalized capital cost would increase to \$4800/kW and the IRR would decrease to 3%/yr. Each 100% increase in the stack and stack replacement costs compared with the cost assumptions in Table 41 has the effect of lowering the IRR by roughly 2%/yr. This sensitivity analysis suggests that AD-SOFC system may be still economically viable even if SOFC systems can't meet DOE-SECA cost estimate goals in the short-term, provided that they can achieve biomass-to-electricity system efficiencies of ~60% and keep down the cost of the AD and sulfur removal equipment.

6.5 Discussion and comparison with alternative technologies

To see how these values of IRR compare with other options for generating electricity from biogas, we estimated costs and efficiencies for internal combustion engines (ICE) and micro gas turbines (mGT). We estimated values of efficiencies for ICE and mGT equipment using the estimate from Cigolotti *et al.* [177], who conducted a techno-economic comparison between sending biogas from an AD to a reciprocating engine, a micro gas turbine or a molten carbonate fuel cell (MCFC). They calculated a biogas-to-electrical efficiency of 33% for the ICE, 24% for the micro GT, and 50% for the MCFC. In order to compare these biogas-to-electricity efficiencies with the exergy efficiencies calculated earlier, these values should be multiplied by 80% in order to account for the 20% exergy destruction associated with conversion of the waste biomass into biogas. This yields exergy efficiencies of 26% for the ICE, 19% for the micro GT, and 40% for MCFC, as compared with the 58% efficiency for the pressurized SOFC. It should be noted that at the scale of 1 MW, gas turbines are less efficient than internal combustion engines, but at scales greater than 100 MW, the reverse is typically true.

In 2008, Cigolotti *et al.* [177] estimated capital costs to be 900 euro/kW for the ICE, 1300 euro/kW for the micro GT, and between 3000 and 4500 euro/kW for the MCFC. They calculated that the pay

back times for each system were 6 yr for ICE, 9 yr for GT and ~4 to 7 yrs for MCFC. Here, we assume the same values of exergy efficiency, and used values of \$1000/kW for the ICE and \$1400/kW for the micro GT, but we did not analyze the MCFC case. Assuming these values of capital costs as well as the same costs for the AD, hydrocyclone, H₂S removal, and EPCC factor, we calculated a value of normalized capital cost of \$9200/kW in 2010 US\$ for the AD-ICE system and \$12,600/kW in 2010 US\$ for the AD-mGT system. These values are two to three times higher than the normalized capital costs of the AD-SOFC system, in large part because the values of exergy efficiency are 2 to 3 times less than the efficiency of the SOFC in converting the exergy of the biogas into electricity.

Assuming the same values for construction time (1 yr), operating time (20 yr), sale price of electricity (\$80/MWh), maintenance cost (\$20/MWh), and capacity factor (80%), we calculated that the IRR of the AD-ICE system to be -1%/yr and the IRR of the AD-mGT system to be -3%/yr. These values of IRR suggest that AD-ICE and AD-mGT systems are not economically viable if the sale price of electricity is only \$80/MWh. Figure 34 shows the IRR as a function of the sale price of electricity for the three ways of generating electricity at a wastewater treatment plant discussed here. The AD-SOFC system maintains a positive value of IRR even at prices of electricity around \$60/MWh. On the other hand, the AD-mGT case does not achieve positive values of IRR even at prices of electricity as high as \$100/MWh.



Figure 34: IRR vs. Sale Price of Electricity for three possible methods of electricity generation at a wastewater treatment plant. The uncertainty in the IRR for each case is on the order of $\pm 4\%/yr$. 'AD-SOFC' = biogas sent to a pressurized solid oxide fuel cell. 'AD-Piston' = biogas sent to a reciprocating piston engine. 'AD-mGT' = biogas sent to a micro gas turbine.

6.6 Conclusions

We conclude that there will likely be economically viable ways of generating electricity at wastewater treatment plants using an anaerobic digester coupled with a pressurized SOFC once there is mass production of SOFC technology even if the cost of SOFC stack materials are significantly greater the DOE/SECA cost targets. This suggests that, in the not-too-distant future, wastewater treatment plants could be converted into net generators of electricity rather than net consumers of electricity. The capital costs were estimated using DOE-SECA targets as the baseline for the cost to mass produce SOFC stacks. While there is large uncertainty in the capital costs of such fuel cell power plants, these results suggest that AD-SOFC systems may be economically viable even if the cost of the SOFC stack is double-to-quadruple the DOE-SECA targets, provided that the system can obtain exergy efficiencies near or above 60%. In addition, the AD-SOFC system is significantly more economically viable than systems in which the biogas is sent to internal combustion engines or micro gas turbines, once SOFC systems are mass produced.

Chapter 7 Overall conclusions, modeling assumptions and future work

The main power plant systems analyzed here, which integrates a catalytic gasifier or an anaerobic digester with a pressurized SOFC, appear to be promising routes to generating positive rates of return on investment. Though, there is still a long road ahead for these technologies because (a) neither of these technologies has been demonstrated at the 100's MW commercial scale, and (b) CO₂ regulations are not in place, such that these could compete with NGCC power plants at today's price of natural gas.

There is still a significant amount of research and development required before there could be commercial scale development of 100's MW-scale catalytic gasifiers integrated with SOFCs. Though, in the short-term, the production scale for SOFC technologies can be increased as they are integrated with anaerobic digesters or operated directly on natural gas. Another promising technology in the short-term is to use fixed-bed, CaO-CaCO₃ looping gasifiers/calciners to convert coal and municipal solid waste (MSW) into methane and carbon dioxide. In future work, we plan to analyze the rate of return on investment of this option, and compare the IRR with the values calculated in this thesis. A fixed-bed, CaO-CaCO₃ looping gasifiers/calciners to convert (MSW) into (a) methane, hydrogen, and/or electricity, (b) pipeline quality carbon dioxide, and (c) pre-calcined feedstock appears to be a promising means of

reducing the amount of waste sent to landfills, enhancing oil recovery from existing oils wells, while reducing the carbon dioxide emissions of both the power plant and cement industries.

In addition, while we collected data using molten alkali hydroxides as the capture/catalyst agents, we did not present a system analysis in this thesis which used a molten catalytic gasifier. In future research, we aim to build a system model in which we use the molten catalytic gasifier and regenerate the alkali hydroxides from the alkali carbonate using electrodialysis or other methods. We did not include this system in this thesis in large part because there is still significant uncertainty in the electricity consumption in the electrodialysis method and because the conventional process for converting alkali carbonates into alkali hydroxides involves mixing aqueous alkali carbonates with calcium hydroxide at low temperatures. The temperature of the regeneration process does not match well with the temperature of the gasification process. While the process described above is unlikely to be able compete against the CaO-CaCO₃ process presented in this thesis, it could be an interesting system to analyze in future research once there is more published data on the electricity consumption of this particular electrodialysis process.

We now focus on the assumptions in modeling sub-systems in the power plants, and how these assumptions can be corrected in the future to decrease the gap between real systems and the fairly simple models used in this thesis. For example, all of the chemical reactors (gasifiers, calciner, H₂S capture vessels) except the anaerobic digester, all of the heat exchangers except Rankine condensers, all of the compressors/turbines, and the SOFCs were assumed to be adiabatic with respect to the outside environment. In other words, I assumed that there is no heat exchange with the outside environment (i.e. heat loss to the outside environment.) While it is possible to design and to construct heat exchangers, compressors, turbines and reactors that are adiabatic with respect to the environment by wrapping the equipment in layers of thermal insulation, it should be noted that this is not always done at actual power plants or chemical plants because the use of thermal insulation has a tendency to increase the amount of time required to maintain the equipment, and hence increases yearly O&M costs. This means that the values of exergy efficiency calculated in this thesis are likely higher than what could be achieved in the actual power plant in which compressors, turbines, heat exchangers, and gasifiers are likely not to be fully covered in thermal insulation. Removing the assumption of adiabatic sub-systems, and/or increasing the O&M costs to reflect the added work to maintain fully insulated equipment, is one the goals of future work.

In addition, one goal of future work is to more accurately model gas compressors and gas turbines. In this thesis, compressor and turbines were assumed to be adiabatic, constant specific heat, and with a given value of isentropic efficiency between 75% and 85%, depending on the scale. (See Appendix E for further details on how compressors and turbines were modeled in this thesis.) Using these three assumptions, modeling compressors and turbines is relatively straight forward. However, (a) real compressors and turbines are not adiabatic because some heat is lost to the environment; (b) the value of the specific heat is likely not constant between the inlet and outlet; and (c) the isentropic efficiency is likely not independent of the pressure or the temperature of the compressor/turbine. As such, the amount of power generated or consumed by turbines and compressors will likely be off by a percent compared to the amount of power generated or consumed by commercially-available turbines and compressors. It should be noted that in all subs-systems in the power plant, except the compressors and turbines, I used an assumption that the specific heat of a gas was a function of temperature. (See Table 42 for the values of the c_p versus temperature used in this thesis.) However, in the compressors and turbines, it was assumed that the compression or expansion occurred rapidly, such that the specific heat of the gas was frozen-in. This "frozen-in assumption" is used extensively to model compressors and turbines because it greatly simplifies the mathematics and because vibrational-modes of gases are known to equilibrate very slowly; however, the kinetic and rotational modes can equilibrate quickly, and therefore, the assumption of constant specific heat can sometimes be a poor assumption for gas turbines and compressors. In future work, I plan to develop improved methods of modeling the power generation/consumption, the heat loss to the environment, and the outlet temperature of turbines/compressors given an inlet temperature and a required pressure ratio.

Another goal of future work is to more accurately model the pressure drops in equipment. For example, as listed in the chapters, pressure drops were estimated in the anode and cathode of the SOFC and in the combustor of gas turbines; however, pressure drops were not included in the other pieces of equipment in the power plants, such as heat exchangers, piping between equipment, and chemical reactors. As such, this is one of the major areas to improve upon in order to more actually model these systems.

However, with these assumptions in mind, it's important to point out as far as conducting economic analyses and as far as trying to teach thermo-economic analysis to future researchers in this field, the largest sources of uncertainty in these power plant designs are not from the thermodynamic assumptions, such as adiabatic reactors or constant specific heat in the compressors/turbines. The largest sources of uncertainty are the capital cost estimates. While a lot more effort could be spent on better models of compressor and/or turbines, the best way to improve upon the work in this thesis is to obtain more accurate cost estimates for the technologies that are still far from mass production (such as SOFCs, ITM, and H₂ membranes) and more accurate cost estimates for the today's power and chemical plants. The large fluctuations in materials costs between 2005-2013, due in part to large fluctuations in oil/gas prices and market bubbles, mean that many of the cost estimates in this thesis may not be valid using standard consumer price inflation indexes. Researchers, including myself, who use data in this thesis should first attempt to find more recent cost estimates from industry, and only if this does not work, then they should attempt to scale cost estimates in this thesis into future dollar costs using a chemical plant cost index, such as the CEPCI.

While there are always ways of going into more layers of detail when conducting cost estimates of power plants, the main disadvantage of more detailed cost estimates is that it is often hard pull-out lessons learned for other engineers to use in future models of similar systems. One lesson learned that I wish to convey to future SOFC designers is the range of values of air stoichiometry, pressure and current density that will likely yield the maximum IRR and minimum LCOE. This is information will likely be useful for both systems designers as well as researchers conducting R&D on SOFC materials.

Appendix A: Make-up of chemicals in calcium looping cycle

This appendix pertains to the CaO looping gasifier/calciner. Here, we estimate the amount of make-up CaO and KOH that would be required in order to sell the bleed-stream as input into a cement kiln. As discussed in the introduction, Weimer *et al.* [36] estimated that the bleed stream would have to be large enough to meet requirements at typical cement kilns for <10%wt CaSO₄ and <30%wt ash. In general, the amount of lime depends on (a) how much carbon capture is required, (b) the ash/sulfur content of the coal, (c) the degradation rate of the lime, (d) the initial capture percentage, and (e) the maximum amount of ash/sulfur.

We made a few simplifying assumptions in order to estimate where the sulfur requirement or the ash requirement would be more restrictive on the amount of required make-up catalyst. If we ignore the amount of ash in the coal and allow the sulfur to be the limiting cause for purging, the equation for the amount of make-up CaO plus CaCO₃ as a function of the amount of carbon in the coal is the following:

Purge fraction $\approx X \cdot [Y - Z/(2X)]$

where X is the molar ratio of sulfur in the coal to the sulfur limit at the cement kiln, Y is the initial molar capture fraction, and Z is the degradation rate per cycle. For the Wyodak-Anderson coal with 0.6% wt sulfur and the <10% CaSO₄ requirement, the value of X is equal to 26%. From our prior experimental research [86], the value of Y was approximately 80% and the value of Z was roughly 3% per cycle. This means that if one ignores the ash content, the purge fraction of lime and hence make-up fraction of limestone is on the order of 18% of the amount of total lime going around the process. In order to meet the requirement that the CaSO₄ content of the purge stream is less than 10% of the solids mixture, the lime can only go through roughly 6 cycles on average before being purged. Note that this is the main reason why we only collected results out to 6 cycles. Note also that if Pittsburgh#8 coal (a 2% wt coal) had been used instead of Wyodak-Anderson coal (a 0.6wt% coal), this 10% wt CaSO₄ limitation would limit the cycle ability of CaO to 2 cycles. An ideal fuel for such a CaO-CaCO₃ cycle would have to be very low in sulfur content if the bleed-stream were to be sold to a cement kiln as a pre-

calcined feedstock.

If instead we ignore the amount of sulfur in the coal and allow the ash to be the limiting cause for purging, the equation for the amount of make-up CaO plus $CaCO_3$ as a function of the amount of carbon in the coal is the following:

Purge fraction $\approx W \cdot [Y - Z/(2W)]$

where W is the molar ratio of ash in the coal to the limit set by the cement kiln, where ash here means the acid components of the ash, such as silica-aluminates and iron oxides. The value of W for the Wyodak-Anderson coal and a requirement of <30% ash is roughly 15%. This means that if one ignores the sulfur content, the purge fraction of lime and hence make-up fraction of limestone is on the order of 11% of the amount of total lime going around the process. In order to meet the requirement that the silica, alumina, and iron content of the purge stream is less than 30% of the solids mixture, the lime can only go through roughly 9 cycles on average before being purged. This means that, as in the case brown coal case studied by Weimer *et al.* [36], the sulfur limit is more restrictive than the ash limit.

We now estimate the cost of CaCO₃ and KOH required as make-up and the potential sale price of the pre-calcined clinker feedstock relative the price of coal. These values were used in the economic analysis of the CaO looping gasifier SOFC system presented earlier. Using the conservative estimate of 20% wt purge of the lime, this means that for every ton of Wyodak-Anderson coal, there needs to be roughly a bleed stream of 0.35 ton of CaO/ash from after the regenerator. Assuming a coal price of \$20/ton and a pre-calcined feedstock of \$40/ton, this means that the sale price of pre-calcined feedstock is roughly 70% of the cost of the coal. Based off of this purge amount, there needs to be a make-up stream of roughly 0.63 ton of CaCO₃ and 0.043 ton of KOH for every ton of Wyodak-Anderson coal entering the gasifier. Assuming limestone costs of \$20/ton and potassium hydroxide costs of \$1000/ton, this means that the ratio of limestone cost to coal cost is roughly 63% and the ratio of the potassium hydroxide cost to coal cost is roughly 210%. The sale of the pre-calciner clinker/ash would likely offset the cost of the limestone required for this process. The use of KOH would increase the yearly material costs; however, the increase is justified by the roughly three-fold increase in the gasification rate when the coal, lime and potassium hydroxide are mixed together aqueous before gasification. For example, the IRR of CaO-looping IGFC system in Chapter 3 decreases by 4%/yr if KOH is not added to the gasifier. Even though the yearly materials costs decrease, the gasifier would need to be 3 times larger, and this caused the overall IRR to decrease, which justifies the use of KOH to increase gasifier kinetics.

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Appendix B: Potential methods of removing hydrogen sulfide and siloxanes

This appendix pertains to the AD-SOFC system. Here, we analyze the various routes to removing sulfides and siloxanes that are present in biogas, and discuss the rationale behind our choice of sulfide and siloxane removal processes. The following is a list of possible routes to remove sulfur, as outlined by various authors such as Krich *et al.* [224], Monteleone [225], and Alptekin *et al.* [226]: (1) addition of air to the AD to convert H₂S to elemental sulfur; (2) caustic scrubbing inside of the AD with sodium hydroxide or lime; (3) caustic scrubbing outside of the AD with sodium hydroxide or lime; (4) activated carbon or physical solvents outside of the AD; (5) Ferric chloride addition to the digester; (6) reaction with iron oxide inside of the AD; and (7) reaction with iron or zinc oxide at relatively high temperature outside of the AD.

We first present in Figure 35 an Eh vs. pH diagram, using HSC Chemistry 6.0 (Outotec, Espoo, Finland), at the temperature of the AD to show the dominant sulfur and carbon species as a function of oxygen concentration (Eh) and proton concentration (pH). Anaerobic digesters typically operate near an Eh value of -0.4 V and a pH value of 7, which is just within the H₂O limits at this value of pH. We can see from Figure 35 that oxygen addition to form sulfur is quite difficult due to the limited range of stability of solid sulfur as a function of Eh and pH. It should be noted that Eh also goes by the term oxygen reduction potential (ORP.) The range of ORP and pH where elemental sulfur is stable is not in the range of ORP and pH where methane is the lowest energy state of carbon. This can be seen by calculating the Gibbs free energy of the reaction of elemental sulfur with methane and liquid water.

$$4 S + CH_4(g) + 2 H_2O(l) = 4 H_2S(g) + CO_2(g) \qquad \Delta G(55^{\circ}C) = -17 \text{ kJ/mol}$$
(40)

This equation suggests that oxygen addition into the AD is thermodynamically more likely to convert methane to carbon dioxide than to convert hydrogen sulfide into elemental sulfur. Adding small amounts of oxygen to low temperature anaerobic digesters could convert hydrogen sulfide; however, when the temperature of the anaerobic digester is above 20°C, the ΔG of the equation above is less than zero. Therefore, we rule out the use of air addition to reduce the H_2S composition. It should be noted that a similar phenomena occurs in coal gasifiers; nearly all of the methane, hydrogen and carbon monoxide must first be oxidized before hydrogen sulfide can be oxidized to elemental sulfur.



Figure 35: Eh vs. pH diagram for (a) sulfur and (b) carbon species at 55°C and 0.1 MPa

Figure 35 also shows that, in theory, sulfur species can be captured inside of anaerobic digester by increasing the pH towards 8. An additive often used in coal gasifiers to capture hydrogen sulfide is lime and/or limestone [79]. However, this reaction has a positive Gibbs free energy only at temperatures below 500 °C. In Eq. (18), we give the H₂S capture reaction and the change in the Gibbs free energy at the temperature of the AD, and in Figure 36, we present the ORP vs. pH diagram for (a) calcium (b) carbon and (c) sulfur species at 55°C and 0.1 MPa.

$$H_2S(g) + CaCO_3 = CaS + H_2O(1) + CO_2(g)$$
 $\Delta G(55^{\circ}C) = +61 \text{ kJ/mol}$ (41)



Figure 36: Eh vs. pH diagram for (a) calcium (b) carbon and (c) sulfur species at 55°C and 0.1 MPa

Both the value of the Gibbs free energy and the results in the ORP vs. pH diagram in Figure 36 show that calcium sulfide is not thermodynamically stable under anaerobic digester conditions. Lime addition to the AD can only capture hydrogen sulfide from escaping in the biogas by increasing the pH above 8.0. Another well known sulfur capture agent is sodium carbonate. However, the change in the Gibbs free energy at the temperature of the AD for this capture reaction is positive. This means that any sodium hydroxide added to the anaerobic digester is more likely to capture carbon dioxide than hydrogen sulfide.

$$H_2S(g) + Na_2CO_3(aq) = Na_2S(aq) + H_2O(l) + CO_2(g) \qquad \Delta G(55^{\circ}C) = +12 \text{ kJ/mol}$$
(42)

$$H_2S(g) + HCO_3^{-1}(aq) = HS^{-1}(aq) + H_2O(l) + CO_2(g)$$
 $\Delta G(55^{\circ}C) = 0 \text{ kJ/mol}$ (43)

However, as mentioned in the main text, adding capture agents into the anaerobic digester that alter the pH can have a detrimental effect on the kinetics of the anaerobic digester. Liu *et al.* [207] determined that the optimal pH for either mesophilic or thermophilic digestion is roughly pH 7.2. For example, an increase in the pH from 7.2 to 8.0 caused a threefold decrease in the cumulative methane production and a decrease in pH from 7.2 to 6.0 caused a roughly twofold decrease in cumulative production. Similar results by other authors [207, 227-229] have showed that the most favorable range of pH to attain maximal biogas yield in anaerobic digestion is 6.5–7.5, which is outside the range in which hydrogen sulfide can be captured by adding caustic agents, such as lime or sodium hydroxide. Though, it should be noted that lime or sodium hydroxide are likely to be required to maintain the pH near 7, in order to compensate for the creation of organic acids during this anaerobic fermentation process. Since attempts to capture sulfur in the anaerobic digester by increasing the pH will have a significantly negative effect on kinetics and capital costs, we ruled out these caustic additives, and next considered iron chlorides as additives.

While the addition of iron chlorides to the anaerobic digester is one means of keeping hydrogen sulfide out of the biogas, it is not a particularly cost effective means of removing the sulfide from the biogas stream. Using chlorides of iron to capture sulfide species has been demonstrated by Dezham *et al.* [203], and is thermodynamically viable:

$$2\text{FeCl}_3 + 3\text{H}_2\text{S}(g) = \text{Fe}_2\text{S}_3 + 6\text{HCl}(aq)$$
 $\Delta G(55^{\circ}\text{C}) = -262 \text{ kJ/mol}$ (44)

$$2\text{FeCl}_3 + 3\text{H}_2\text{O}(1) = \text{Fe}_2\text{O}_3 + 6\text{HCl}(aq)$$
 $\Delta G(55^\circ\text{C}) = -120 \text{ kJ/mol}$ (45)

However, since one of the end products of this reaction is hydrochloric acid, one would also have to add in basic materials (i.e. caustic materials, such as lime or sodium carbonate) in order to neutralize the pH. Given the price of iron chloride and caustic per ton, this is not an economically viable option compared with the other options discussed below.

We now turn to the chosen means of bulk removal of sulfides from entering the biogas, which is the addition of iron (III) oxides directly into the AD. In Figure 37, we show the Eh vs. pH diagram for (a) iron, (b) sulfur and (c) carbon species at 55°C and 0.1 MPa. In Eqs. (23), we present the Gibbs free energy of reaction for the relevant capture reaction inside of the AD.



Figure 37: Eh vs. pH diagram for (a) iron, (b) sulfur and (c) carbon species at 55°C and 0.1 MPa

$$Fe_2O_3 + 3H_2S(g) = Fe_2S_3 + 3H_2O(l)$$
 $\Delta G(55^{\circ}C) = -142 \text{ kJ/mol}$ (46)

Figure 37 as well as Eq (23) show that iron oxide can be added to the AD to capture hydrogen sulfide. Since these iron sulfides are insoluble, the addition of iron oxide should not have a significant effect on the pH of the AD. The advantage of using additives inside of the AD is that capital costs can be reduced compared with *ex situ* capture equipment, and that some additives that capture sulfur could be beneficial to the anaerobic digestion process by providing additional sources of chemical exergy to the bacteria. As highlighted in the main text, Kato *et al.* [206] recently found that the addition of electrically conductive forms of iron oxide can have a significantly positive effect on the rates of methanogenesis. Therefore, iron oxide addition is unlikely to reduce the sulfide concentration in the biogas to less than 1 ppm. Therefore, external sulfide removal is required as well as iron oxide addition to the AD.

There are a number of commercial processes for capturing hydrogen sulfide from natural gas. These processes include the following: (1) activated carbon [230]; (2) capture by sodium hydroxide and regeneration of the sodium hydroxide via iron redox processes, such as LO CAT® (Merrichem, Houston, TX) or ThiopaqTM (Shell-Paques, The Hague, Netherlands) [231]; and (3) physical solvents, such as Selexol® (UOP LLC, Des Plaines, IL.) The use of physical solvents and activated carbon can be easily ruled out for capture from biogas because the biogas is not at high enough pressures for physical solvents to work efficiently. The Lo-Cat and/or Paquel iron redox process may be of interest because it has been demonstrated on natural gas stream at temperature on the order of 50°C with H₂S concentration on the order to 2000 ppm; however, the demonstrated pressures were on the order of 5 MPa to 8 MPa, well above the range of pressures that would make economic sense at an AD-SOFC system.

Since commercial processes have been designed for high pressure gas streams, we decided to go with non-commercial technologies, such as iron oxide addition into the anaerobic digester and the zinc oxide process still being developed by RTI In. and Eastman Chemical [232, 233], which promises to achieve H₂S levels below 1 ppm using a regenerative zinc oxide-sulfide two-fluidized bed and which was described in detail earlier in the main text.

Appendix C: Definition of exergy

The exergy of a system is the maximum useful work during a process that brings a system into equilibrium with its environment. Exergy exists in multiple forms, such as electro-chemical exergy, gravitational exergy, thermal exergy, kinetic exergy or mechanical exergy. One form of exergy can be converted into another form of exergy with 100% efficiency only for some very simple, ideal reversible processes. Since almost all processes involve irreversible processes (diffusion, chemical reaction, etc.), exergy is not conserved; and conversion of one type of exergy into another form of exergy is <100%. Due to irreversible processes, the exergy of a closed system always decreases.

The molar flow exergy, $\hat{\varepsilon}$, of a substance entering or exiting a control volume is the following

Exergy of a Control Volume

$$\hat{\varepsilon} = (\hat{h} - \hat{h}_0) - T_0(\hat{s} - \hat{s}_0) + \sum_i x_i (\hat{\mu}_i - \hat{\mu}_{i_0})$$

Where \hat{h} is the molar enthalpy of the substance at the temperature, T. Where \hat{h}_0 is the molar enthalpy of the substance at the temperature of the environment, T₀, (~300 K for most processes on Earth.) Where \hat{s} is the entropy of the substance at (T,p), \hat{s}_0 is the entropy of the substance at (p_o, T_o). p_o is the total pressure of the environment, p is the total pressure of the fluid, $\mu_{o,i}$ is the chemical potential of species i at (T_o, x_i ·p), and $\mu_{env,i}$ is the chemical potential of species i at (T_o, p_{env}), where p_{env} is the partial pressure of the species in the environment.

This definition of exergy ignores the gravitational potential energy and directed kinetic energy. Both of these terms should be included in the equation above if the terms are relevant to the problem. For fuel cell systems, it is often safe to ignore gravity and the directed kinetic energy of the fluids. You can include this terms by replacing \hat{h} in the top equation with $\hat{h} + mgh_{cm} + \frac{1}{2}m\bar{v}^2$, where m is the mass per mole of substance, h_{cm} is the height of the center of mass of the control volume above a reference height, and \bar{v} is the directed velocity of the control volume. We will ignore these terms for the fuel cell systems of interest. In order to calculate the change of enthalpy and entropy from state 1 to state 2 for an ideal gas, one needs to know the specific heat at constant pressure as a function of temperature. The figure below shows the specific heat at constant pressure (normalized by the universal gas constant) as a function of the temperature of the gas for some of the main constituents of fuel cell systems.



Specific heat at constant pressure of various gases

The specific heat of a gas is an increasing function of the temperature of the gas. Note that the specific heat at constant pressure of a monotonic gas is equal to $\frac{5}{2} R$. Each degree of translational motion yields $\frac{1}{2} R$ towards the specific heat. For diatomic and polyatomic gas species, we need to include the rotational and vibrational modes. If the temperature of the gas is much larger than the characteristic energy of a certain rotational or vibrational mode, then each rotational mode available contributes $\frac{1}{2} R$ towards the specific heat and each vibrational available mode contributes **1** *R* towards the specific heat. If the temperature than the characteristic energy of a certain rotational or vibrational available mode contributes **1** *R* towards the specific heat. If the temperature of the gas is much smaller than the characteristic energy of a certain rotational or vibrational or vibrational available mode contributes **1** *R* towards the specific heat is mode contributes **0** *R* towards the specific heat. In the temperature range of interest for most systems, the specific heat can be approximated with a linear fit, i.e. the specific heat is approximately equal to a constant plus some linear function of temperature.

$$c_p \approx c_p^{300K} + \beta \cdot (T - 300 \, K)$$

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Using the approximation of an ideal gas mixture and the approximation of linearly-varying specific heat, we can solve for $\hat{h} - \hat{h}_o$, $\hat{s} - \hat{s}_o$, and $\mu_{o,i} - \mu_{env,i}$:

$$\hat{h} - \hat{h}_o = \left(c_p^{300K} - \beta \cdot T_o\right) \cdot \left(T - T_o\right) + \frac{1}{2} \cdot \beta \cdot \left(T^2 - T_o^2\right)$$
$$\hat{s} - \hat{s}_o = \left(c_p^{300K} - \beta \cdot T_o\right) \cdot \ln\left(\frac{T}{T_o}\right) + \beta \cdot \left(T - T_o\right) - R \cdot \ln\left(\frac{p}{p_o}\right)$$
$$\mu_{o,i} - \mu_{env,i} = RT_o \cdot \ln\frac{p_o}{p_{i,env}}$$

Using these formulas, we obtain the following equation for the molar flow exergy of a mixture:

$$\hat{e}(\chi_{i}, T, p, T_{0}, p_{0}) = \sum_{i} \chi_{i} \cdot \left[\left(c_{p}^{300K} - \beta \cdot T_{0} \right) \cdot \left[(T - T_{0}) - T_{0} \cdot ln \left(\frac{T}{T_{0}} \right) \right] + \frac{1}{2} \cdot \beta \cdot (T - T_{0})^{2} + RT_{o} \cdot ln \frac{p_{i}}{p_{i,env}} \right]_{i}$$

Table 42: The values of c_p^{300K}, β , $p_{i,env}$ for each of the main gas species.

Species	Atmospheric Partial	Chemical Potential at	C_p^{300K}	β
(Italics = not	Pressure at Chemical	1 atm (For reference		
used in	Equilibrium, <i>p_{i,env}</i>	only, not used)		
models)	[atm]	[kJ/mol]	[J/mol·K]	[mJ/mol·K ²]
Nitrogen	0.78	0.7	29.1	5
Oxygen	0.21	4.0	29.3	8
Water vapor	0.01 - 0.04	8-12	33.5	11
Argon	0.01	12		
Carbon Dioxide	0.0004	20	37.2	24
Helium	5.10-6			
Hydrogen	10 ⁻⁴¹	235	28.6	2
Carbon Monoxide	10 ⁻⁴⁷	275	29.1	6
Methane	10 ⁻¹⁴⁸	830	35.5	54
Ethane		1485	53.0	104

Exergy Balance & Exergy Destruction Equation

By adding the energy conservation equation (First Law of Thermodynamics) together with the entropy balance equation (Second Law of Thermodynamics) multiplied by T_0 , then one can derive the exergy balance equation:

Energy Conservation Equation (First Law): Open System

$$\frac{dU_{cv}}{dt} = \sum_{i=input} \dot{n}_i \, \hat{h}_i - \sum_{e=ouput} \dot{n}_e \, \hat{h}_e + \sum \dot{Q} - \sum \dot{W}$$

Entropy Balance Equation (Second Law): Open System

$$\frac{dS_{cv}}{dt} = \sum_{i} \dot{n}_{i} \, \hat{s}_{i} - \sum_{e} \dot{n}_{e} \, \hat{s}_{e} + \sum_{j} \frac{\dot{Q}_{j}}{T_{j}} + \sum \dot{\sigma}_{irr}$$

Exergy Balance Equation for an Open System

$$\frac{dE_{cv}}{dt} = \sum_{i} \dot{n}_{i} \, \hat{e}_{i} + \sum_{k} \left(\frac{T_{k} - T_{0}}{T_{k}} \right) \dot{Q}_{k} - \dot{W}_{useful} - T_{0} \cdot \dot{\sigma}_{irr}$$

For a fuel cell systems, the non-control volume work is typically just the electrical energy that leaves the fuel cell or turbine. For a steady state process, the exergy balance equation becomes the following:

$$\dot{W}_{elec} = \sum_{i} \dot{n}_{i} \, \hat{e} + \sum_{k} \left(\frac{T_{k} - T_{0}}{T_{k}} \right) \dot{Q}_{k} - T_{0} \cdot \dot{\sigma}_{irr}$$

 \dot{W}_{elec} is the electrical power produced by the fuel cell plus any work generated by a turbine and minus any work consumed by compressors or pumps. The electrical power produced by the fuel cell is equal to the difference in electrical potential at the anode versus the cathode times the current of electrons moving through that potential. Irreversible processes decrease the amount of power actually generated by fuel cell systems.

Exergy is destroyed by irreversible processes. The rate of exergy destruction, $\dot{\Phi}_{des}$, is equal to $T_0 \cdot \dot{\sigma}_{irr}$. This is called the Gouy-Stodola Theorem. The rate of loss of work potential is equal to the temperature of the environment times the generation rate of entropy due to irreversible processes.

$$\dot{\Phi}_{des} = T_o \cdot \dot{\sigma}_{irr}$$

A fuel cell is a device that converts a portion of the chemical energy of a fuel directly into electrical energy. A chemical fuel is fed to the anode electrode and a chemical oxidant is fed to the cathode electrode. In order to continuously produce electricity, a fuel cell needs a continuous supply of both fuel and oxidant. The overall reaction between hydrogen and oxygen inside a fuel cell is shown below:

$$H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(g \text{ and/or } l)$$

The overall reaction is always separated into two half reactions. For example, the reaction of hydrogen and oxygen to form water (vapor and/or liquid, depending on the temperature of the fuel cell) is composed of two half reactions (the half reactions depend on the type of fuel cell.) For a solid oxide fuel cell (SOFC), the anode half reaction is:

$$H_2(g) + O^{2-}(ionic) \leftrightarrow H_2O(g) + 2e^{-}$$

For the SOFC, the cathode half reaction is:

$$\frac{1}{2}O_2(g) + 2e^- \leftrightarrow O^{2-}(ionic)$$

The figure below shows a schematic of the operation of a SOFC.



The definition of the anode electrode of a fuel cell is the location where the fuel is oxidized (i.e. where electrons are produced in the half reaction and leave the system to go to an external load.) The definition of the cathode electrode of a fuel cell is the location where the oxidant is reduced (i.e. where electrons enter the system from the external load and are consumed in a half reaction.) Electrochemical reactions are heterogeneous (i.e. occur at an interface and require a three-phase boundary between gas, electrolyte & electrode)

SOFC Open Circuit Voltage

We can calculate the open circuit potential of a SOFC by deriving it from first principles. Hydrogen molecules react with oxygen ions (O^{2-}) in the ceramic electrolyte near the anode electrode:

$$H_2(g) + O^{2-}(ionic) \leftrightarrow H_2O(g) + 2e^{-}$$

This produces a local increase in the concentration of electrons and a local decrease in the concentration of oxygen ions. Since the oxygen ions can diffuse through the ceramic electrolyte of the SOFC, the anode begins charging up negatively (from the build-up of electrons) and the cathode begins charging up positively (from the build-up of ytrrium (Y^{3+}) and zirconium (Zr^{4+}) positive ions for a YSZ electrolyte.) An electric field is produced that counteracts the diffusion of the oxygen ions. Eventually, a steady-state is reached in which the current is exactly zero:

Current Density =
$$i = 0 = \left(z_{O2-} \cdot F \cdot D_{O2-} \cdot \frac{dc_{O2-}}{dx}\right) + \left(\sigma_{O2-} \cdot \frac{d\varphi}{dx}\right)$$

Note that the ionic conductivity, σ , is closely related to the ionic diffusivity, D.

$$\sigma_{02-} = \frac{(F \cdot z_{02-})^2 \cdot D_{02-} \cdot c_{02-}}{RT}$$

$$z_{02-} \cdot F \cdot D_{02-} \cdot \frac{dc_{02-}}{dx} + \left[\frac{(F \cdot z_{02-})^2 \cdot D_{02-} \cdot c_{02-}}{RT}\right] \frac{d\varphi}{dx} = 0$$

Dividing by $(z_{02-} \cdot F \cdot D_{02-} \cdot c_{02-})$, and rearranging yields:

$$RT\frac{d\ln(c_{O2-})}{dx} + (F \cdot z_{O2-})\frac{d\varphi}{dx} = 0$$

Adding a constant within the first derivative and rearranging, this becomes:

$$\frac{d}{dx}\left[RT \cdot ln\left(\frac{c_{O2-}}{c_{O2-}^o}\right)\right] + \frac{d}{dx}\left[F \cdot z_{O2-} \cdot \varphi\right] = 0$$

The first term is the spatial derivative of the chemical potential, and the second term is the spatial derivative of zF times the electrical potential. This equation becomes:

$$\frac{d}{dx}(\mu_{02-} + F \cdot z_{02-} \cdot \varphi) = 0$$

And therefore we can see that, under open circuit conditions, the electrochemical potential of the protons is a constant throughout the electrolyte.

$$\frac{d}{dx}\overline{\mu}_{O2-}=\mathbf{0}$$

Or by integrating across the electrolyte, one obtains the open cell potential across a PEM fuel cell:

$$\mu_{02-}{}^{anode} + F \cdot z_{02-} \cdot \varphi^{anode} = \mu_{02-}{}^{cathode} + F \cdot z_{02-} \cdot \varphi^{cathode}$$

Rearranging this yields:

$$\varphi^{cathode} - \varphi^{anode} = \Delta \varphi = \frac{\mu_{02-}{}^{anode} - \mu_{02-}{}^{cathode}}{Fz_{02-}}$$

$$\Delta \varphi = \frac{RT}{Fz_{02-}} ln \left(\frac{c_{02-}^{anode}}{c_{02-}^{cathode}} \right)$$

The ratio of the oxygen ion concentration at the anode to cathode is proportional to the pressure of oxygen at the anode and the cathode:

$$\frac{c_{O2-}^{anode}}{c_{O2-}^{cathode}} = \left(\frac{p_{O2}^{anode}}{p_{O2}^{cathode}}\right)^{1/2}$$

$$\Delta \varphi = \frac{RT}{F z_{O^{2-}}} ln \left(\frac{p_{O2}^{cathode}}{p_{O2}^{anode}}\right)^{1/2} = \frac{RT}{4F} ln \left(\frac{p_{O2}^{cathode}}{p_{O2}^{anode}}\right)$$

The oxygen pressure at the anode is related to the gibbs free energy of formation of water from hydrogen and oxygen.

$$K(T) = e^{-\Delta G_f/RT} = \frac{a_{H2O}^{anode}}{a_{H2}^{anode} \cdot (a_{O2}^{anode})^{1/2}} \approx \frac{(p_{H2O}^{anode}/1 \ atm)}{(p_{H2}^{anode}/1 \ atm) \cdot (p_{O2}^{anode}/1 \ atm)^{1/2}}$$

Remembering to divide the pressures by 1 atm (which is the pressure at which the gibbs free energy of formation was taken), we can solve for the oxygen pressure at the anode:

$$(p_{O2}^{anode})^{1/2} = \frac{p_{H_2O}^{anode}}{e^{-\Delta G_f/RT} \cdot p_{H_2}^{anode}}$$

Using this value of the pressure of oxygen in the anode, one obtains:

$$\Delta \varphi = \frac{-g_{f,H2O(g)}(T, 1 atm)}{2F} + \frac{RT}{2F} ln \left[\frac{p_{H2}^{anode} \cdot (p_{O2}^{cathode})^{1/2}}{p_{H2O}^{anode}} \right]$$

This equation is the equation used to estimate the open circuit voltage of SOFCs in chapters 3,4 and 6. The values of the partial pressure of the gases was taken to be the average of the inlet and the outlet partial pressure.

Irreversibility in SOFCs

The actual voltage across the anode and cathode of fuel cell is equal to:

$$V = \Delta \varphi - \sum \eta = \Delta \varphi - \eta_{act,a} + \eta_{act,c} + \eta_{ohmic} + \eta_{conc,a} + \eta_{conc,c}$$

where $\Delta \varphi$ is the open circuit potential and $\sum \eta$ is the sum of all of the overpotentials due to irreversible processes, i.e. finite kinetics. The two main sources of irreversibly in SOFC fuel cell stacks are: (1) electro-chemical reactions and (2) charge diffusion. The irreversibility of the electro-chemical reactions is due to the finite reaction rates, due to an activation barrier. Typically, there is one rate-limiting elementary reaction on each side of the fuel cell. The activation barrier for this rate-limiting reaction can be lowered by 'spending' voltage, i.e. having a gradient in the electrochemical potential.

The current at either electrode can be calculated using the Butler-Volmer equation, which is a function of the electrode overpotential:

$$i = i_o^0 \left(\frac{\prod c_R}{\prod c_R^0} \cdot e^{\alpha z F \eta / RT} - \frac{\prod c_P}{\prod c_P^0} \cdot e^{-(1-\alpha) z F \eta / RT} \right)$$

Where t_o^0 is the exchange current density when the concentration of species is equal to the concentration of species at open circuit conditions, c_R is the concentration of reactants, c_R^0 is the concentration of reactants at open circuit conditions, c_P is the concentration of products, c_P^0 is the concentration of products at open circuit conditions, alpha is a symmetry factor describing the shape of the activation barrier near its peak, z = the number of electrons transferred in the rate-limiting step, $\eta = \eta_{act}$ is the activation overpotential (cathode/anode), and RT is the temperature of the fuel cell in J/mol. Typically, the symmetry factor is assumed to be $\frac{1}{2}$ (describing a perfect parabola at the peak of the activation barrier), and then the αz or $(1-\alpha)z$ are combined, and called the transfer coefficient (Think of it as a variable describing molecules interacting at the peak of the activation barrier, and it is dimensionless.) The variable measures the probability of falling left/right times the number of charges produced/consumed when falling left/right. For SOFCs, the value of αz for the cathode is typically 2, and the value of αz for the anode is typically 1.

$$\eta_{B-V}^{activation} \approx \frac{RT}{\alpha zF} ln\left(\frac{i}{i_o^0} + 1\right)$$

This equation must be applied to both the anode and cathode electrodes, i.e. there is a separate value of (αz) and i_o^0 for both the anode and cathode. What remains the same is the temperature, *T*, and the current density, *i*. For SOFC cathodes, the value of the exchange current density is on the order of 10^{-2} A/cm². For SOFC cathodes, the value of the exchange current density is on the order of 10^{-1} A/cm².

The other major source of irreversibility in SOFCs is diffusion of ionic species through the electrolyte (i.e. charge diffusion.) An ionic species encounters an enormous number of small activation barriers as it travels through the electrolyte (whether the electrolyte is a water-filled polymer or a ceramic.) While the size of the activation barrier is small compared to the activation barrier of typical chemical reactions, the total irreversibility (and hence exergy destruction) can be large because there are so many encounters with the small activation barriers. At each activation barrier at which the ionic species has just enough energy to reach the top of the barrier, there's a roughly 50%/50% probability of it either going over the barrier, or going back to where it came from. This randomization of the position and velocity is irreversible, and leads to exergy destruction (a way of turning directed energy into thermal energy.) This source of irreversibility is called the ohmic overpotential.

$$\eta_{ohmic} = i \cdot ASR = \frac{i \cdot L}{\sigma} = I \cdot R$$

Where *i* is the current density $[A/cm^2]$ and *ASR* is the area specific resistance $[\Omega \cdot cm^2]$, *I* is the total current [A], $\sigma [\Omega^{-1} \cdot m^{-1}]$ is the ionic conductivity, *L* [m] is the length of the electrolyte, and *R* $[\Omega]$ is the total resistance of the electrolyte. By including both of the main sources of overpotential in SOFCs, one can calculate the actual fuel cell voltage as a function of the current density, the temperature and the partial pressures of the gas species.

$$V = \Delta \varphi \left(p_{H2}^{anode}, p_{O2}^{cathode}, p_{H2O}^{anode}, T \right) - \frac{RT}{\alpha z F} ln \left(\frac{i}{i_o^0} + 1 \right) - i \cdot ASR(T)$$

Appendix E: Modeling of the balance of plant equipment

A. Compressors/Turbines:

The independent variables for modeling an adiabatic compressor or a turbine are the following: a) the inlet temperature, T_{inlet} , b) the pressure ratio, $\frac{p_{exit}}{p_{inlet}}$, and c) the isentropic efficiency, η . Once you know these three variables, then you can solve for all of the other variables that would need to calculate, such as the exit temperature, the power, or the exergy destruction. The isentropic efficiency, η , of a compressor or turbine is a measure of the amount of exergy destruction. When η is equal to 0% for a turbine, then there is no work that can be generated by the turbine. When η is equal to 0% for a compressor, then there is an infinite amount of work that would be required to achieve a given pressure ratio. The value of η , of a compressor or turbine is unique to the device of that device, and can vary widely between various manufacturers. Sources of entropy generation inside of a compressor or turbine include: a) gradients in momentum due to wall friction and b) heat flow due to gradients in temperature.

Typical compressor and turbines have isentropic efficiencies around 70-90%. This means that they do not operate reversibly, and instead, there is internal generator of entropy within the compressor and turbine. The irreversibility is mostly due to momentum diffusion, but in some cases, thermal diffusion becomes significant. Using the First Law & Second Law as well as assuming the equipment is adiabatic (i.e. no heat transfer to the surroundings) and steady state conditions, we can derive the following equations for the power and entropy generated in a turbine or the power consumed in a compressor:

$$\dot{W}_{elec} = \dot{n} \cdot \left(\hat{h}_{inlet} - \hat{h}_{exit} \right)$$

$$\dot{\sigma}_{irr} = \dot{n} \cdot (\hat{s}_{exit} - \hat{s}_{inlet})$$

The power generated or consumed is given by flow rate of the gas times the change in the actual enthalpy of the gas. If we can assume that the gas in the compressor or turbine is ideal and has a constant specific heat, then the power generated or consumed is:

$$\dot{W}_{elec} = \dot{n} \cdot c_p \cdot (T_{inlet} - T_{exit}) = \dot{n}c_p T_{inlet} \cdot \left(1 - \frac{T_{exit}}{T_{inlet}}\right)$$

This means that we can calculated the power generated or consumed by just knowing the temperature before and after the compressor/turbine. The ratio of the exit to inlet temperature is a function of the pressure ratio and the isentropic efficiency. If the isentropic efficiency is equal to one, then the ratio of the exit to inlet temperature is:

$$\frac{T_{exit}}{T_{inlet}} = \left(\frac{p_{exit}}{p_{inlet}}\right)^{\frac{R}{c_p}}$$

This equation can be derived from a second law balance and assuming the following: 1) adiabatic (i.e. no heat transfer to surroundings), 2) ideal gas, and 3) constant specific heat. When there are irreversible processes, then the ratio of the exit to inlet temperature must be determined by using the definition of the isentropic efficiency.

$$\eta^{compressor} = \frac{\hat{h}_{outlet}^{ideal} - \hat{h}_{inlet}^{ideal}}{\hat{h}_{outlet}^{actual} - \hat{h}_{inlet}^{actual}} = \frac{\left(\left(\frac{p_{exit}}{p_{inlet}}\right)^{\frac{R}{c_p}} - 1\right)}{\left(\frac{T_{exit}}{T_{inlet}} - 1\right)}$$

$$\eta^{turbine} = \frac{\hat{h}_{outlet}^{actual} - \hat{h}_{inlet}^{actual}}{\hat{h}_{outlet}^{ideal} - \hat{h}_{inlet}^{ideal}} = \frac{\left(1 - \frac{T_{exit}}{T_{inlet}}\right)}{\left(1 - \left(\frac{p_{exit}}{p_{inlet}}\right)^{\frac{R}{c_p}}\right)}$$

The definition of the isentropic efficiency of a compressor is the ratio of the ideal change in enthalpy over the actual change in enthalpy. And the definition of the isentropic efficiency of a turbine is the ratio of the actual change in enthalpy over the ideal change in enthalpy. The terms on the right hand side of each of the equations make the additional assumptions of ideal gas and constant specific heat. These equations can be re-arranged to solve for the ratio of the exit to inlet temperature for a turbine or compressor that is not isentropic.

For a given pressure ratio, the temperature behind an actual compressor is greater than the temperature behind an ideal, reversible compressor. The actual temperature is given by the equation below, and is function of the inlet temperature, the pressure ratio, the isentropic efficiency, η , and the specific heat of the gas.





A similar equation can be derived for the temperature after a turbine. The temperature at the exit of a turbine with irreversibility is higher than the temperature at the exit of an isentropic turbine.





Using these temperature ratios, we can calculate the power output or input:

$$\dot{W}_{elec}^{turbine} = \dot{n} \cdot c_p \cdot T_{inlet} \cdot \eta^{turbine} \cdot \left[1 - \left(\frac{p_{exit}}{p_{inlet}}\right)^{\frac{R}{c_p}}\right]$$

$$\dot{W}_{elec}^{compressor} = \frac{\dot{n} \cdot c_p \cdot T_{inlet}}{\eta^{compressor}} \cdot \left[1 - \left(\frac{p_{exit}}{p_{inlet}}\right)^{\frac{R}{c_p}} \right]$$

The exergy destruction is equal to the flow rate times the temperature of the environment times the change in entropy of the gas.

$$T_{0} \cdot \dot{\sigma}_{irr} = \dot{n} \cdot T_{0} \cdot \left[c_{p} \cdot ln\left(\frac{T_{exit}}{T_{inlet}}\right) - R \cdot ln\left(\frac{p_{exit}}{p_{inlet}}\right) \right]$$

For the turbine, the exergy destruction becomes:

$$T_{0} \cdot \dot{\sigma}_{irr} = T_{0} \cdot \dot{n} \cdot \left\{ c_{p} \cdot \ln\left(1 - \eta^{turbine} \cdot \left[1 - \left(\frac{p_{exit}}{p_{inlet}}\right)^{\frac{R}{c_{p}}}\right]\right) + R \cdot \ln\left(\frac{p_{inlet}}{p_{exit}}\right) \right\}$$

When the isentropic efficiency is equal to one, it is clear from the equation above that the exergy destruction is equal to zero, and when the isentropic efficiency is equal to zero, the exergy destruction is equal to $RT_o \cdot ln\left(\frac{p_{inlet}}{p_{exit}}\right)$, which can be considered to be equal to the pressure exergy lost via unconstrained expansion through the "0% efficient turbine," i.e. through an expansion valve. Note that the exergy destruction through the turbine or compressor is independent of the inlet temperature. The exergy destruction, for a given flow rate of gas, is only a function of the pressure ratio and the isentropic efficiency.

Note that the equations that contain c_p assume that the specific heat is equal to a constant and assume that there is only gas species. If there the gas is a mixture, it is easy to correct the c_p used in the equations above. $c_p = \sum_i \chi_i \cdot c_{p,i}$

B. Heat Exchangers

Heat exchangers in solid oxide fuel cell systems are typically used to bring the inlet gases to the SOFC to a high enough temperature to avoid forming local cold spots that can cause the ceramic materials to break. For example, if room temperature gases directly entered the SOFC, there would be a local cold spot at the entrance, and there would be a significant gradient in temperature between the inlet and the outlet. This temperature gradient would most likely lead to the destruction of the ceramic due to thermal stresses (due to uneven expansion of the material.)

Heat exchangers in PEM fuel cell systems are most used to condense water from the cathode exhaust so that some of the water can be used to humidify the inlet gas streams. Or this can be done via a membrane that allows water vapor to pass through from the high humidity exit stream to the low humidity inlet stream. Other uses of heat exchangers in PEM fuel cell systems include: a radiator to cool the coolant used to maintain the fuel cell temperature below 100 °C.

There are two main types of heat exchangers: co-flow and counter-flow. Of the two types, counterflow heat exchangers are generally preferred for the following reasons: 1) the exit temperature on the cold side of the HX can reach high temperatures and 2) the size and hence the capital cost of the HX is generally smaller. All heat exchangers used in this thesis were counter-flow heat exchangers.



For any given heat exchanger, there are typically two input temperatures and two output temperatures. But since there is only one equation (the first law, i.e. the second law introduces a new variable, $\dot{\sigma}_{irr}$, so it won't help solve for the exit temperatures), then there must be one external constraint in order to solve for the exit temperatures. Normally, this constraint is either the required goal for the outlet temperature on the cold side or a minimum value for the pinch point temperature between the hot and cold sides. The constraint for the HX's in a SOFC is typically the temperature of the gas entering the SOFC. This must be in a narrow range of possible temperatures. So, using the First Law, we can solve for the exit temperature on the hot side of the HX:

$$0 = \sum_{i} \dot{n}_{i} (\hat{h}_{inlet} - \hat{h}_{outlet})_{i}$$

$$\dot{n}_h (\hat{h}_{inlet} - \hat{h}_{outlet})_h = \dot{n}_c (\hat{h}_{outlet} - \hat{h}_{inlet})_c$$

The outlet temperature on the hot side of the HX is a function of the two inlet temperatures and the constrained outlet temperature on the hot side. As in the case of turbines and compressors, it is important to sue the correct value of c_p . For gas mixtures, use the sum of the mol-fraction χ_i times the $c_{p,i}$ of each species. Once we know this temperature, we can solve for the internal generation of entropy using either the second law balance or the exergy balance equation. It is generally easily to use the second law balance here.

By multiplying the second law balance equation by T_o and eliminating terms that are zero, the exergy destruction for a heat exchanger is given by the following (assuming no heat transfer to the surroundings, ideal gas, constant specific heat and no pressure drop):

$$T_{0} \cdot \dot{\sigma}_{irr} = \dot{n}_{h} \cdot T_{0} \cdot c_{p,h} \cdot \ln\left(\frac{T_{outlet}}{T_{inlet}}\right)_{h} + \dot{n}_{c} \cdot T_{0} \cdot c_{p,c} \cdot \ln\left(\frac{T_{outlet}}{T_{inlet}}\right)_{c}$$

The total heat exchanged between the two sides is given by:

$$\dot{Q} = \dot{n}_h \cdot c_{p,h} \cdot (T_{inlet} - T_{outlet})_h = \dot{n}_c \cdot c_{p,c} \cdot (T_{oulet} - T_{inlet})_c$$

Given the equation above for the exergy destruction, we can see that the exergy destruction normalized by the amount of heat transfer is given by:

$$\frac{T_0 \cdot \dot{\sigma}_{irr}}{\dot{Q}} = \frac{T_0}{(T_{inlet} - T_{outlet})_h} \cdot \ln\left(\frac{T_{outlet}}{T_{inlet}}\right)_h + \frac{T_0}{(T_{outlet} - T_{inlet})_c} \cdot \ln\left(\frac{T_{outlet}}{T_{inlet}}\right)_c$$

Now, we will define the following "log-mean" quantities on the hot and cold sides:

$$T_{h}^{LM} = \frac{(T_{outlet} - T_{inlet})_{h}}{\ln\left(\frac{T_{outlet}}{T_{inlet}}\right)_{h}} \qquad T_{c}^{LM} = \frac{(T_{outlet} - T_{inlet})_{c}}{\ln\left(\frac{T_{outlet}}{T_{inlet}}\right)_{c}}$$

Therefore, the normalized exergy destruction is equal to:

$$\frac{T_0 \cdot \dot{\sigma}_{irr}}{\dot{Q}} = \left(\frac{T_0}{T_c^{LM}} - \frac{T_0}{T_h^{LM}}\right) = \frac{T_0 \cdot (T_h^{LM} - T_c^{LM})}{T_c^{LM} \cdot T_h^{LM}}$$

In the case of a HX that exchanges heat between two sides at near infinite temperatures, we obtain the result that the exergy destruction is nearly zero, which makes sense because the thermal energy is transferred from gas with a Carnot efficiency of ~1 to a gas with a Carnot efficiency of ~1. We also see that the exergy destruction is equal to zero when $T_h^{LM} \cong T_c^{LM}$. This could be the case for a counterflow heat exchanger where the inlet temperature of the hot side is equal to the outlet temperature of the cold side and vice versa. There is virtually no driving force for heat exchange, and therefore this HX would be nearly infinite in size (area) or would require a material that had a near infinite heat conductivity. Either way, the capital cost for this HX with virtually no exergy destruction would be much higher than for a HX with greater exergy destruction. You must know the capital cost of the HX's in order to determine which is the optimal HX for generating the highest overall rate of return on investment. And this will be the subject of the next section. Before moving on, we should note that according to the equation above, the exergy destruction of a counter-flow HX is the same as the exergy destruction of a co-flow HX if the inlet and exit temperatures are the same. This makes sense because the exergy balance equation treats what happens inside of the HX like a black box whose only inputs are the temperatures at the outlets and inlets. If these are the same, then the exergy destruction is the same. Though, we should note here that the size of the co-flow HX is larger than the counter-flow HX for the same inputs and outputs. We will now show why this is the case.

We first start out by defining the log mean temperature difference, LMTD:

$$LMTD = \frac{\Delta T_{Side1} - \Delta T_{Side2}}{ln \left[\frac{\Delta T_{Side1}}{\Delta T_{Side2}}\right]}$$

Where ΔT_1 and ΔT_2 are defined as in the diagram above. Note that this is <u>not</u> the same as $T_h^{LM} - T_c^{LM}$. The LMTD is the log-mean difference in temperature between the two sides. Using Fourier's law, we can calculate the exchange of heat across the HX as a function of the LMTD.

$$\dot{Q} = \binom{k}{d} \cdot LMTD \cdot A \qquad [W]$$

Where *k* is the thermal conductivity of the material separating the two fluids, $[W/(m \cdot K)]$, *d* is the length of material separating the two fluids, and *A* is the area of the HX. For the same \dot{Q} , *k*, and *d*, then the area of the heat exchanger is inversely proportional to the LMTD.

Material	Thermal Conductivity at 300 K	
	[W/mK]	
Aluminum	250	
Carbon Steel	50	
Stainless Steel Generic	16	
Stainless Steel 316	13	

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